Reappraisal of Tannery Effluents: Implications for Treatment

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of

Master of Technology

By

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to the

Environmental Engineering and Management Programme

Indian Institute of Technology Kanpur

KANPUR – 208016, INDIA

January 2005

Certificate

This is to certify that the work contained in the thesis titled: *Reappraisal of Tannery Effluents: Implications for Treatment,* by *Mr Prabhat Kumar Singh* has been carried out under my supervision.

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January 2005

7/1/05

Dedicated to… … …

my family and friends

Acknowledgement

I would not been where I am today: brimming with confidence, highly oriented and with elevated energy level without continuous guidance, and sage suggestion received from my thesis supervisor Dr Vinod Tare to accomplish this thesis. It has been an immense pleasure for me to acknowledge him for his generous way of teaching, holding a meeting at proper interval, giving full freedom and positive criticism that has really restructured my outlook. I owe a great respect and honor for him to endorse my first journey of research.

I was fortunate to receive important guidance from Dr Chaudhauri, Dr Ghosh, Dr Sharma, Dr Boss, Dr Guha and Dr Rath throughout the course work and otherwise. They were always accessible and understanding whenever I approached them.

I am grateful to Mishraji, R. B. Lal and Vijay for their help in the laboratory. It would not have been possible to carry out the experiments without their active support.

I would like to express my sincere thanks to UP Jal Nigam, Kanpur and Unnao Tanneries Pollution Control Company Limited to allow me to conduct pilot-scale experiments and their co-operation at all levels. Thanks are due to Central Pollution Control Board (CPCB), Kanpur, Central Leather Research Institute (CLRI), Kanpur and State Pollution Control Board, Kanpur for providing valuable data and suggestions.

I am highly indebted to Ajay Kanaujia and his wife Anu for their help and to provide accessibility to their laboratory to perform experiments at Jajmau. The help rendered by Manoj at Unnao is highly appreciable. It would not be possible for me to conduct experiments at such a large levels without the help receive from my two field assistant Santosh and Mamu to run the setup properly and very sincerely without any of my much guidance. Their sincerity and understanding way is highly appreciable.

A Sincere thanks to all my colleagues Abhinaya, Amita, Arun, Bhawana, Bharati, Deepti, Devendra, Indrani, Leena, Major Sir, Rajveer, Shrawan and Subhankar. A lot of thanks to my seniors Satwat Sir, K D Sir, Alok Sir,

Gunjan, Yash, Narendra, Kamlesh and Amit. In addition, I would express my thanks to project persons Rajveer, Arvind, Harishankar, Dilip, Ravindra and my juniors Antra and Reddy.

I take the opportunity to express my sincere gratitude to Manoj Tiwari for taking care of my reactors in my absence and help provided, to Arun for his assistance in operating TOC machine and boost for everything and I am highly obliged to Rinku for his help in formatting and editing thesis write-up.

I am thankful to God for giving the friend like Phoolendra Mishra, Manoj Tiwari, Saurabh Srivastwa, Gaurav Bhatt, Arun Kumar, Rahul Singh, Palvi Singh Patel and Suchitra Saxena, who always stands with their support, motivation, guidance and criticism at all the way of my life.

The chain of my gratitude would be definitely being incomplete if I would forget to thank the first cause of this chain my parents, sister and other family members for their unconditional love, care and moral support. I would like to specially thank to Prerna Pant for her love and care through out my thesis work.

Last but not the least, I would like to express my gratitude to all my well wishers, the names of whom I have failed to include in this thesis acknowledgement.

Prabhat K Singh

Place : IITK
Date : Feb 09, 2005

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Abstract

The genesis of the present research was the reported poor performance of an Upflow Anaerobic Sludge Blanket (UASB) based Common Effluent Treatment Plant (CETP) for the treatment of tannery effluents. Review of literature revealed that the poor performance is generally attributed to the failure of chrome recovery units and primary treatment, and poor operation and maintenance. In this research it was postulated that the failure is due to the inappropriate application of process concept, and that the conventional biological processes have insignificant potential for the treatment of tannery effluents. As such the present study was directed to: (i) investigate if application of UASB process for tannery effluents is appropriate considering the characteristics of the tannery effluents reaching the CETP, (ii) reappraisal of the tannery effluents to investigate if the characteristics have significantly altered over a period of time since the inception of the concept of UASB in CETPs due to possible change in practices in tanneries, (iii) assess the potential of commonly used biological processes for treatment in CETPs for tanneries, (iv) to evaluate the prospects of anaerobic digestion in CETPs of primary sludge from tanneries, and (v) suggest plausible means of treatment. The results indicate that, in general in tannery effluents, much of the organic matter present is in suspended form and very small amount is present in soluble form. The conventional approach to apply aerobic suspended growth systems or upflow anaerobic sludge blanket process appears to be inappropriate. Also, the primary sludge is not amicable to anaerobic digestion, perhaps due to sulfide toxicity. Much of the oxygen demand, and hence reported high values of BOD, of the anaerobic effluents appears to be due to the presence of sulfides and does not necessarily indicate presence of high amount of biologically degradable organics. It is suggested that the CETPs for tanneries may explore anaerobic digestion of primary sludge after dewatering to remove substantial portion of sulfate and sulfide or attempt vermicomposting of primary sludge after chromium removal by mixing with other organic matter such as animal dung or agricultural wastes for reuse and recovery of resources.

Keywords

Common Effluent Treatment Plants, Biological Processes, Upflow Anaerobic Sludge Blanket, Activated Sludge Process, Aerobic Suspended Growth, Tannery Effluents, Primary Treatment, Chromium Removal, Vermicomposting.

1. Prologue

Tanneries are reported to occupy significant position in terms of Indian exports and employment opportunities to the people of economically weaker section. However, sustenance of tanneries, particularly of small units, is becoming increasingly difficult due to alarming levels of environmental pollution created by different tanning operations and practices currently used. While the big units can manage to utilize recent tools for proper environmental management such as process change towards cleaner production, waste minimization, etc., smaller units are still starving to adopt end of the pipe solutions such as the installation of effluents treatment plants. A lot of efforts have been made for appropriate treatment of tannery effluents.

The treatment of tannery effluents at individual tanneries is considered to be difficult because most of tanneries lack availability of land, adequate financial supports and reasonable technology to combat with the challenges. In general, the concept of common effluent treatment plant (CETP) after chrome recovery and pre-treatment at individual tanneries is gaining popularity. Aerobic (Activated Sludge Process, ASP) and anaerobic (Upflow Anaerobic Sludge Blanket, UASB) biological processes are being used for the treatment of tannery wastewaters. In Kanpur, Uttar Pradesh, India, under the Ganga Action Plan Phase I (GAP I), a 36 mld (million liters per day) wastewater treatment plant to treat 9 mld effluents from some tanneries in Jajmau area by mixing it with 27 mld domestic wastewater has been commissioned with the assistance of the Government of Netherlands based on UASB process. The plant has been operational since 1994. Another CETP, treating only tannery effluents is situated in the neighboring town Unnao, Uttar Pradesh, India. This plant is based on ASP.

Several studies reveal that the performance of the 36 mld UASB based plant at Jajmau is poor (Tare, 2004; Qureshi and Dixit, 2003; Tare *et al.*, 2003; Rajeswari, 1998). The amount of biogas generated is much below the expected levels. The performance of the ASP based CETP at Unnao appears to be satisfactory as claimed by the plant operators (Tare *et al.*, 2003).

In general, poor performance of UASB based plant is attributed to (i) improper design, operation and maintenance, (ii) toxicity to methanogens due to either high levels of sulfides or chromium, and/or (iii) significant difference between the estimated design and actual characteristics of the tannery effluents. This study was initiated to probe further into the causes of failure of UASB based plant for treatment of tannery effluents. Emphasis was laid on reappraisal of tannery effluents and to assess the potential of biological treatment of organics present.

2. Literature Review

2.1 Scope

Concerns over the environmental degradation and the demand for the safe disposal of industrial wastes are the topics of current interest. The leather industry is associated with the generation of huge amounts of liquid wastes (30-35 l/kg of raw material processed) and thus the disposal of these waste becomes a serious problem. It is well documented that the technologies used for the treatment of such wastes are not meeting the standards, and also not cost effective. Therefore, there is fundamental need to go for improved technology to combat with the problem of treatment of tannery wastewaters. In this review emphasis is placed on the practices for the management of liquid effluents from tanneries and their suitability and sustainability.

2.2 General

India is one of the largest producers of leather. The annual earnings from the leather goods are estimated to exceed Rupees 70 billion. The leather industry in India, in general, is spread all over the country, but typically concentrated in some clusters in the states of Tamil Nadu, Uttar Pradesh, West Bengal, Punjab, and Maharashtra. The process of manufacturing leather is called tanning, and requires a large quantity of water and several chemicals to convert raw hides/skin into leather. A very small fraction of the chemicals and water forms a part of the final products. As such tanneries generate a large amount of wastewater that contains several unused chemicals, suspended and soluble organic matter removed from hides/skin causing high BOD and COD. In addition, the tanneries are responsible for generating solid and hazardous waste, and fugitive sources of obnoxious odors causing substances.

Despite being hazardous and highly polluting, tanneries in India continue to get political support due to their substantial share in export earnings and direct employment to people belonging to economically weaker section of the society. The risk due to unsafe practice of discharge of waste poses challenges to sustain tanning industries without any danger to environment. Most of the small tanneries face difficulty in installing wastewater treatment plant due to constrains on finances and availability of land.

To overcome these difficulties, the concept of common effluent treatment plants, CETPs, after primary treatment by individual tanneries has been advocated by various agencies. A lot of work has been carried out at laboratory, pilot and field scale with various technological options and management strategies on CETPs for a cluster of tanneries. Conflicting views have emerged on the performance and impact of the implementation of CETP scheme. The choice of technology adopted in CETP vis-à-vis the claims made regarding its environmental impact in abating the pollution is a matter of debate. The present work was initiated to assist in addressing the issues related to the choice of treatment technology for treatment of tannery wastewater.

2.3 Characteristics of Tannery Effluents

Tanning is the process of converting animal hides/skins into leather. The tanning process can be broadly classified into two types - vegetable tanning and chrome tanning. This classification is basically done on the type of tanning agent. In case of vegetable tanning, Babool bark is used besides other chemicals. For chrome tanning, basic chrome sulfate is used besides other chemicals. The processes used for the tanning of hides in the most of the tanneries include soaking (removal/release of salts used for curing /preserving the hides), liming (reaction with hydrolyzed lime solution and sodium sulfide) and defleshing (removal of unwanted flesh and hair). To neutralize the excess lime in hides, deliming process is carried out, wherein hides are treated with an acid salt like ammonium chloride. After the deliming, the hides are pickled with sodium chloride and sulphuric acid followed by the tanning process (CPCB, 1996).

Tanning process generates a large volume of liquid wastes. Liquid wastewater is produced during soaking, liming, pickling, bating, and tanning operations. Volume and characteristics of different streams of wastewater in tanneries depends on the process and practice adopted. Khanna *et* al. (1994) have documented sources, quantities and characteristics of wastewater from different operations in tanneries based on collation of information available from a number of studies within and outside India. By and large tanneries effluents are reported to contain substantial quantities of suspended and dissolved solids, sulfates and sulfides; and cause high BOD and COD. In 1988, Centre Leather Research Institute (CLRI) carried out survey

of tanneries in Kanpur to predict the quantity of wastewater produced, characteristics, and diurnal variation of wastewater quality. 5 out of total 179 tanneries were selected for monitoring purpose. The wastewater produced and its characteristics in different processes were measured and based on the findings, the volume of wastewater produced and its characteristics for whole area were predicted. The characteristics of tannery wastewater as predicted by CLRI are presented in Table 2.1. The parameter values, in general, fall well within the range reported by various other studies summarized by Khanna *et al.* (1994).

Table 2.1: Characteristics of Tannery Wastewater at Jajmau, Kanpur
(Source: UP Jal Nigam, 1991)

Parameter	Value
pH	8.2-9.2
Alkanity, mg/L as $CaCO_3$	2000-2750
Total BOD, mg/L	1950-3100
Soluble BOD, mg/L	1670-2600
Total COD, mg/L	4500-7500
Soluble COD, mg/L	3000-4800
Total solids, mg/L	25000-37000
Chlorides, mg/L	10770-14900
Sulfate, mg/L	1540-3300
Chromium, mg/L	160-275

2.4 Recovery of Chromium from Tannery Effluents

Recovery of chromium in individual tanneries has been strongly advocated (Khanna *et* al., 1994). The spent chrome tan liquor is segregated from the other streams and is collected in a holding tank. It is then pumped to reaction-cum-settling tank. Magnesium oxide is added to the tank, and mixed, and contents are allowed to settle at the hopper bottom of the tank. Settled chromium hydroxide is withdrawn into the sludge dissolving tank. Concentrated sulphuric acid is added to the tank for dissolving chromium hydroxide. The final product obtained is in the form of $Cr(OH)SO_4$. The recovered chromium is in liquid form and can directly be used in tanning operation. A properly designed and operated recovery plant can remove up to 98% of the

chromium in the spent liquor (Unnao Tanneries Pollution Control Company, 1998). While a number of tanneries have installed chrome recovery plants, continuous and sustained operation is doubtful, and hence large quantities of chromium is found in the wastes that leave the tannery premises (Rajeswari, 1998).

2.5 Treatment of Tannery Effluents

Tannery effluents are typically treated in two stage treatment. The first stage, referred as primary treatment, involves simple settling after addition of chemicals for neutralization and/or chrome recovery. The second stage, referred as secondary treatment, involves biological processes - considered to be compatible with nature's way of assimilating the pollutants and are also found to be the most economical means of treatment of waste that contain degradable organics. Biological wastewater treatment processes are generally classified into two broad categories viz. aerobic and anaerobic from the aspect of final electron acceptors in the degradation of organic matter. These two processes have several advantages and disadvantages when compared with each other. For example, the aerobic treatment processes produce better effluent quality in shorter retention time, but require more energy and produce more sludge. The advantages of aerobic treatment become the disadvantage of anaerobic treatment and vice versa.

2.5.1 Anaerobic Treatment

In developing countries, due to financial constraints, selecting low cost treatment system that involves least mechanical and electrical equipment and energy consumption is very important for sustainable operations. It has been argued that conventional wastewater treatment systems used in developed countries can not be successfully used in developing countries due to high energy requirements and constraints in stable maintenance. Hence emphasis is given on employing anaerobic reactors that recover energy in the form of biogas from wastes.

Recent developments in reactor configuration design combined with better understanding of the microbiology of anaerobic systems have substantially increased the effectiveness of anaerobic treatment systems. In certain situations it is considered to be a good alternative to the aerobic systems. The problem of large reactor volume in anaerobic systems has been overcome by the introduction of immobilized systems

in which a long biological solids retention time can be maintained for a short hydraulic retention time (HRT). Among the various immobilized anaerobic systems, the Upflow Anaerobic Sludge Blanket (UASB) reactor is one of the most effective systems. Its good treatment efficiency and cost effectiveness led to adoption of UASB process in a common effluent treatment plant (CETP) at Jajmau, Kanpur, Uttar Pradesh (UP), India. The plant was commissioned in 1994. The plant is designed to treat 9 mld effluents from tanneries located in Jajmau by dilution with 27 mld Kanpur city sewage.

While it is claimed that UASB technology is one of the most viable technologies for treatment of wastewaters in tropical countries, it is important to note that performance of the existing plant does not often achieve the expected levels due to variety of problems including improper operation and maintenance. While proper operation and maintenance is an issue for most of the plants, detailed performance studies by various researchers have revealed that anaerobic treatment is not a good option for the treatment of tannery effluents due to the fact that most of the organic matter is in suspended form (Qureshi and Dixit, 2003; Rajeswari, 1998).

The specific characteristics of tannery effluents, having high suspended solids, high COD, BOD, high sulfate, sulfide and chromium make it unsuitable for the anaerobic treatment. It is speculated that chromium present in the tannery effluent may have an adverse impact on methanogenesis. Sulfate reduction under anaerobic condition also poses severe problems to anaerobic treatment of tannery wastewater. Lens *et al.* (1998a) have recently viewed various aspects of biotechnological treatment of sulfate–rich wastewater. Important observations are as follows:

- Major problems of biological treatment of sulfate-rich wastewater are production of H_2S, which cause corrosion, odor, increased effluent COD, and toxicity to microorganisms leading to process failure.
- Selection of the treatment strategy depends on the aim of treatment: (i) removal of organic matter, (ii) removal of sulfate, or (iii) removal of both.
- Addition of extra COD in form of ethanol or synthesis gas (mixture of H_2, CO_2 and CO) is required for the complete removal of sulfate if COD/SO_4^{2-} ratio is lower than 0.67.

- Sulfate can be removed from the wastewater by the coupling of a sulfide oxidation step to a sulfate reduction step. Sulfur can be recovered from wastewater in case H_2S can partially oxidize to insoluble elemental sulfur.
- Sulfide toxicity may be reduced by using methods such as dilution of the influent, controlling reactor pH, sulfide precipitation using iron, sulfide stripping, separation of sulfide production and methanogenesis using two-phase or staged system.

Srinivasan and Veeraraghavan (1998) also reviewed various aspects of anaerobic treatment of high sulfate content industrial wastewaters and observed the following:

- Sulfide is toxic to methane producing bacteria and limits the application of anaerobic treatment to various industrial wastewaters.
- Anaerobic treatment of high sulfate containing wastewater is possible by means of careful control of influent pH and COD/SO_4^{2-} ratio.
- Immobilized reactors showed higher threshold for sulfide toxicity than suspended biomass reactors.

Anaerobic treatment of sulfate-rich wastewaters involves competitive interactions among various group of bacteria including SRB and MPB. A number of factors affect this dedicate ecosystem. These factors include substrate composition and concentration, COD/SO_4^{2-} ratio, sulfate concentration, sulfide levels, immobilization or adhesion property of microorganisms, H_2 partial pressure, trace metals and other nutrient, chelators, vitamin concentration, thermodynamics, proximity of microorganisms (biofilm versus dispersed), temperature, long term population shifts, reactor configuration (Speece 1996), organic loading rate (Choi and Rim, 1991), pH (Koster *et a*l., 1986), proximity of sulfate reduction with respect to methanogenesis, pH gradients (Colleran *et al.*, 1995) and acclimatization (Ish *et al.*, 1986b).

The application of anaerobic digestion technology to sulfate containing wastewaters frequently presents difficulties due to problems of toxicity, reduction of methane yield, malodor and corrosion. Especially problematic is the inhibitory effect of H_2S on several types of anaerobic bacteria involved in the anaerobic digestion. Inhibition decreases the efficiency of reactor performance and can even lead to process failure (Koster *et al.*, 1986; Hilton and Oleszkiewicz, 1988). In general, wastewaters with

COD/SO^{2-}_4 ratio higher than 10 pose no problems for methanogenic treatment (Rinzema and Lettinga, 1988). To date, no models have been developed that allow prediction of the conditions that result in process failure of digesters treating wastewaters with COD/SO_4^{2-} ratio lower than 10. This is largely attributable to lack of investigation on the likely out come of competition between SRB and methane-producing bacteria (MRB). This in turn, determines the amount of sulfide present in the reactor. Knowledge of the factors influencing the outcome of this competition would not only avoid the risk of process failure, but would also allow manipulations, by practical engineering measures of the bacterial conversion routes in order to achieve either completely Methanogenic or completely sulfidogenic operation. Some recent studies reveal that methanogenesis can not be effectively used for wastewaters exhibiting COD/ SO^{2-}_4 ratio lower than 4-5 (Patidar, 2003; Patidar and Tare, 2004a; Patidar and Tare, 2004b; Patidar and Tare 2004c). Efforts to minimize adverse effect of sulfate reductions using inhibitors and modified reactor configurations have not been successful (Patidar, 2003; Patidar and Tare, 2004a; Patidar and Tare, 2004b; Patidar and Tare 2004c).

2.5.2 Aerobic Treatment

A number of studies involving various types of aerobic systems such as oxidation ponds, aerated lagoons, trickling filters, activated sludge processes and its variants, oxidation pond, etc. have been conducted at laboratory, bench, pilot and full scale levels for tannery effluents with or without the primary treatment. A comprehensive documentation describing the outcome of such studies has been prepared by Khanna and coworkers for Ministry of Non-conventional Energy Sources, Government of India, New Delhi (Khanna *et al.*, 1994). A review of this document reveals that varying degree of treatment is achieved using different processes but the effectiveness of biological processes and the contribution due to biological degradation is a matter of speculation and no substantive information can be obtained from the literature in this regard. For example, significantly low levels of MLSS ($\approx$1600 mg/L) in an Oxidation Ditch with 3.5 d retention time for secondary treatment of tannery effluents at Lodygowice suggest insignificant biodegradation (Khanna *et al.*, 1994).

2.6 Comparative Assessment of Aerobic and Anaerobic Treatments

Under the Ganga Action Plan Phase I (GAP I), a 36 mld common effluent treatment plant (CETP) to treat 9 MLD wastewater from some tanneries in jajmau area in Kanpur, UP, India by mixing it with 27 MLD domestic wastewater has been commissioned with the assistance of the Government of Netherlands based on upflow anaerobic sludge blanket (UASB) process. The plant has been operational since 1994. Another CETP treating 2.15 mld based on Activated Sludge Process (ASP) was commissioned in neighboring town Unnao for cluster of 21 tanneries in 1996. Tare *et al.* (2003) report that ASP based plant is superior in all aspects. This conclusion is at variance with the conventional wisdom of the superiority of anaerobic processes for tannery wastewaters in tropical developing countries like India. It must be noted that the performance of ASP based CETP has not been independently assessed and the significance of aerobic biological process is a matter of speculation. ASP based plant gives better effluent in terms of BOD levels compared to UASB. However, that does not imply that organic matter removal occurs in aerobic process compared to the anaerobic process. High levels of sulfides in anaerobic effluents may have contributed to oxygen demand leading to misleading BOD values (Yadav, 2002; Jain, 2003).

2.7 Concluding Remarks

While it is claimed that UASB technology is one of the most viable technologies for treatment of tannery effluents in tropical countries, it is important to note that performance of the existing plants does not often achieve the expected levels due to variety of problems including improper operation and maintenance. Thus it is important to properly operate and monitor the performance of these plants regularly so as to provide insight into various aspects of design, operation and maintenance. This would help to suggest some corrective measures for improving the plant performance and also to suggest modifications in future planning and design.

The comparative assessment of aerobic and anaerobic processes at the secondary level suggests that aerobic processes yield better effluent quality in terms of BOD. However, this may be because of the interference due to sulfate/sulfide and not necessarily due to higher removal of organics in aerobic systems. Thus the true

potential of biological processes needs to be investigated considering the fact that much of the organic matter in tannery effluents is in suspended form.

Several technological advances in the field of both aerobic and anaerobic treatment have significantly improved process operation and economics. Most of the process improvements come from change in engineering aspects rather than fundamental shifts in the underlying microbial principles. Since most of the disadvantages of the aerobic and anaerobic process come from the microbiological principles it is very difficult to expect radial changes as long as the microbial cultures normally associated with the conventional aerobic-anaerobic processes are employed. Thus it is warranted that systems which involve/promote superior microbial ecology be developed to degrade suspended organics present in the tannery effluents.

3. Objective and Protocol

Technologies based on aerobic and anaerobic process are being used and recommended in CETPs for tannery effluents. In general, activated sludge process (ASP) based treatment technologies are considered to be energy intensive and expensive from operation and maintenance point of view. On the other hand anaerobic processes, while claimed to offer several advantageous under tropical climate conditions, are reported to perform poorly due to the presence of certain constituents in the tannery effluents. The selection of the treatment technology in CETP is thus fraught with difficulties due to inadequate information and analysis of available data. Particularly, the potential for conventional biological processes at the secondary level needs to be reinvestigated considering the fact that much of the organic matter present in tannery effluents is in suspended form and very small amount is available as soluble fraction. Thus the main thrust in the present research was on reappraisal of the characteristics of the tannery effluents and the assessment of the potential of conventional biological processes for the treatment of tannery effluents in light of the reported failure or inappropriate application of biological processes. Specifically, the efforts were directed to find answers to some of the following questions.

- Is the failure or underperformance of UASB based CETP at Jajmau, Kanpur, UP, India essentially due to improper design, and poor operation and maintenance?
- Are the characteristics of the tannery effluents reaching the CETP substantially different than those assumed in design due to change in practices in tanneries over past two decades?
- Can the performance of UASB reactor be improved if excessive amount of chromium reaching the CETP is removed through primary settling at the plant?
- Can conventional biological treatment, viz. anaerobic and anaerobic, of settled tannery effluent substantially remove organic load from tannery effluents?
- Is it viable to practice anaerobic digestion of primary sludge at CETP and produce biogas for meaningful applications?
- Is it feasible to eliminate effect of sulfate/sulfide in anaerobic treatment of tannery effluents/sludges?

The genesis of the present study is the investigation for the under performance of the CETP at Jajmau, Kanpur, UP, India and some preliminary studies to remodel the plant for improving the performance (Qureshi and Dixit, 2003). Hence, much of the investigation is focused on estimation of the characteristics of the tannery effluents reaching the CETP and evaluate different schemes using conventional biological process options for the treatment. An attempt has been made to generalize for all the tanneries based on collation of data from literature and some analysis of another CETP based on ASP for a cluster of tanneries in the neighboring town Unnao, UP, India. The study was carried out on following lines.

- Collation of information regarding the performance of CETP for a cluster of tanneries in Jajmau, Kanpur, UP, India since its inception from various sources.
- Generation of performance data for the past several months and preparing typical COD mass balance for summer and winter conditions.
- Reappraisal of the tannery effluents reaching the CETP and comparison with earlier estimates to analyze the changes in characteristics that may affect the plant performance.
- Bench scale column and pilot scale primary treatment of the tannery effluents reaching the CETP to evaluate the effectiveness in removal of organic matter and asses the impact of removal of suspended solids and chromium in subsequent anaerobic treatment.
- Aerobic and anaerobic treatment of settled effluents in laboratory/bench scale experiments to assess the potential of conventional biological processes for tannery wastewaters.
- Bench scale experiments for anaerobic digestion of primary sludge produced from settling tanneries effluents.

4. Methods

4.1 Experimental

The study involved investigation of five different aspects to find answers to the questions posed in the previous chapter, and was accordingly divided into five parts. The first part of the study involved analysis of the historical data on the performance of UASB based CETP at Jajmau, Kanpur, UP, India and collection of performance data independently to carry out the COD mass balance. The second part of the study was carried out to estimate the characteristics of the tannery effluent reaching the CETP to assess the differences in parameter values from those estimated in the design as well as generally reported in literature. In the third part bench and pilot scale experiments were conducted to assess the potential of primary treatment at the CETP for removal of chromium and two other key parameters, viz. TSS and COD. The fourth part of the study involved assessment of the potential of the conventional biological processes, viz. aerobic suspended and UASB for the treatment of settled tannery effluents using laboratory scale models. In the fifth part feasibility of anaerobic digestion and biogas production of the sludge obtained from primary treatment was studied using laboratory scale digesters.

4.1.1 Performance Evaluation of the UASB Based CETP

These studies were carried out for a CETP planned, designed and commissioned for a cluster of tanneries in Jajmau, Kanpur, UP, India. The plant was designed to treat 9 mld tannery effluents in two UASB reactors in parallel by mixing with 27 mld domestic wastewater of Kanpur city. Thus the design capacity of the plant is 36 mld to treat a mixture of tannery effluents and domestic wastewater in the ratio 1:3. This was based on the results of a pilot scale study conducted by Central Leather Research Institute (CLRI) with different combinations of tannery effluents and domestic wastewater (CLRI, 1988). The layout of the plant is given in Figure 4.1.

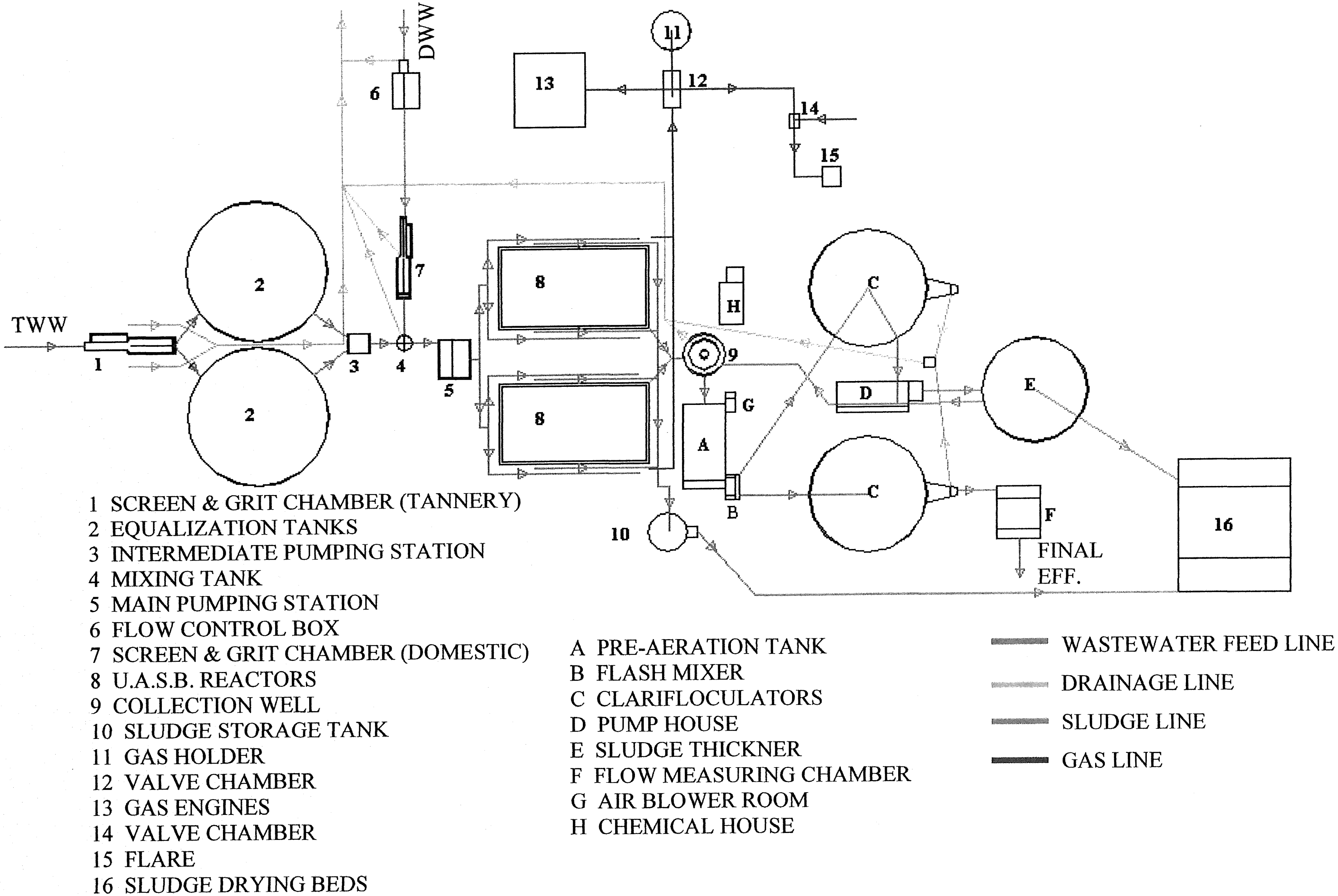


Figure 4.1: General Layout of 36 MLD UASB Based CETP Plant at Jajmau, Kanpur

The plant was commissioned in 1994. Initially the plant was started with domestic wastewater of Kanpur city and gradually the quantity of tannery effluents were increased in steps from 0 to 9 mld.

Several performance monitoring programmes were undertaken during commissioning and after words in the past ten years (Prasad, 1995; Rajeswari, 1998; Tare, 2004). Data from all these studies have been collated. Independent monitoring over a period of one year was also done during July 2003-June 2004. The plant performance was monitored for 3-4 days in a month, generally during 20th to 25th day of the month. The sampling locations chosen included common influent point, i.e. mixing tank where tannery effluents pumped from the equalization tank are mixed with the domestic wastewater, and end of the effluent channels of both UASB reactors (Figure 4.1). Three-hourly grab samples were collected at each sampling locations. A portion of the grab samples was used for estimation of pH, temperature and sulfide at the site, and the remaining was preserved after acidification in the refrigerator till next morning for preparing flow-based composite samples. 24 h composite samples were prepared on a volumetric flow basis at the laboratory attached to the 36 MLD CETP under investigation. The composite samples were daily brought to the Environmental Engineering Laboratory of the IIT Kanpur for analysis of the various parameters. The parameters analyzed included COD (total and soluble), TSS, and VSS. Every month, sludge samples of UASB reactor were also brought to the Environmental Engineering Laboratory of the IIT Kanpur for analysis of the various parameters such as TSS, VSS and Cr. The amount of biogas produced was monitored by noting the rise in gas dome level between the two gas-flaring operations.

4.1.2 Reappraisal of Tannery Effluents

CLRI (1988) had estimated the characteristics of tannery effluents by selecting few representative tanneries and mixing the wastes from various operations in proportion to the quantities produced. Several other reports are also available that describe the characteristics of the tannery effluents (Khanna *et al.*, 1994; Rajeswari, 1998). An independent assessment of the tannery effluents reaching CETP under investigation and

another ASP based CETP in the neighboring town for another cluster of tanneries was carried out.

For UASB based CETP, 20 l sample collected at the outlet of the grit chamber (Figure 4.1) every hour during 07:00 – 19:00 h was transferred into a Raw Tannery Wastewater Sump (RTWW Sump). The contents of the RTWW Sump were thoroughly mixed and used for settling analysis and analysis of various parameters to estimate the characteristics of tannery effluents reaching the CETP. Samples were preserved at low temperature before analysis. This exercise was repeated number of times during February – July 2004.

For ASP based CETP, composite samples were prepared by mixing grab samples collected at 3 h interval during 9:00 – 18:00 h. Compositing was done based on volumetric flow rate measured at the time of collection of grab samples. Samples were preserved at low temperature before analysis. This exercise was conducted four times in a week over a period of two months.

4.1.3 Primary Treatment of Tannery Effluents Reaching CETP

Assessment of the potential of simple settling for the removal of TSS, chromium and corresponding COD was done in two different types of experiments, namely column settling analysis and pilot scale studies. Both studies were carried out at the CETP under investigation using tannery effluents collected in the RTWW sump as mentioned in the previous section.

Column settling analysis was carried out in a Plexiglas column of 1700 mm height and 100 mm diameter (Figure 4.2). Column was filled with tannery effluents collected in the RTWW sump after thorough mixing. Samples were withdrawn every hour from different ports at various time intervals for a period of eight hours and analyzed for TSS.

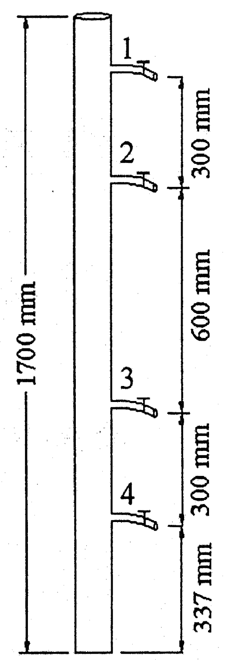
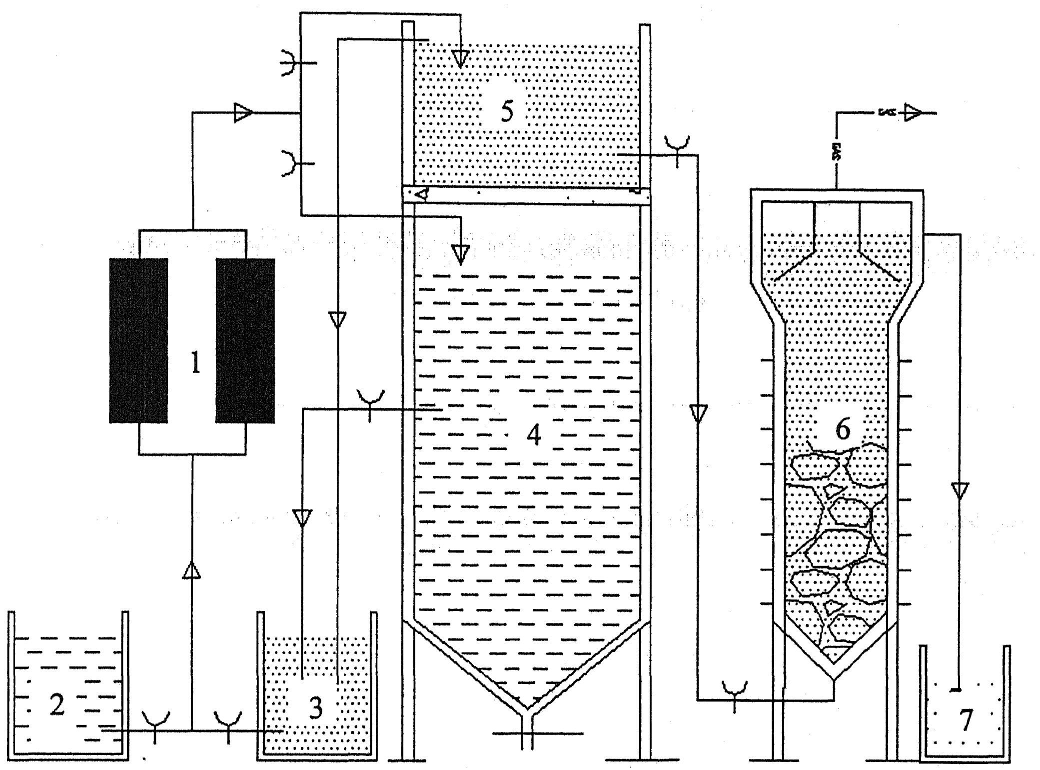


Figure 4.2: Settling Column

A pilot-scale settling tank (Dimensions: 1000 x 1000 x 1800 mm) was constructed near the equalization tank of the CETP to estimate the removal of suspended solids, COD and chromium by simple settling from tannery effluents. It was operated in batch process with Hydraulic Retention Time (HRT) of two to three hours. Tank was filled with tannery effluents collected in the RTWW sump after thorough mixing using pumps (Figure 4.3). Some settling experiments were also conducted on tannery effluents pumped from the sump of intermediate pumping station. In such experiments the TSS levels were observed to be lower than those in the RTWW Sump due to settling of solids in the sump itself.



1: Pump; 2: RTWW Sump; 3: Storage Tank; 4: Settling Tank; 5 Feeding Tank; 6: UASB Reactor; 7: Effluent Collection Tank

Figure 4.3: Experimental Setup of Settling Tank and UASB Reactor

The supernatant of the settling tank, after pre decided HRT, was withdrawn through a nozzle to a storage tank The sludge settled at the bottom of settling tank was removed periodically to avoid biological degradation inside the settling tank. Samples withdrawn

from RTWW sump, storage tank and the sludge were subjected to TSS, VSS, Total and Filtered (TCOD and FCOD), and Cr analysis.

4.1.4 Laboratory Scale Studies Using Aerobic Suspended Growth and UASB Processes

The assessment of the potential of commonly used biological treatment processes for the removal of organic matter from the settled tannery effluents was done using laboratory scale models of aerobic suspended growth and UASB processes as follows.

Aerobic Suspended Growth Reactors: Aerobic reactors, with the main aim to examine the potential of conventional aerobic suspended growth system in removal of organic matter from settled tannery wastewater were setup in laboratory. To accomplish the above, three aerobic reactors (AR-I, AR-II and AR-III) with one liter capacity each, were operated under semi-continuous mode (Figure 4.4).

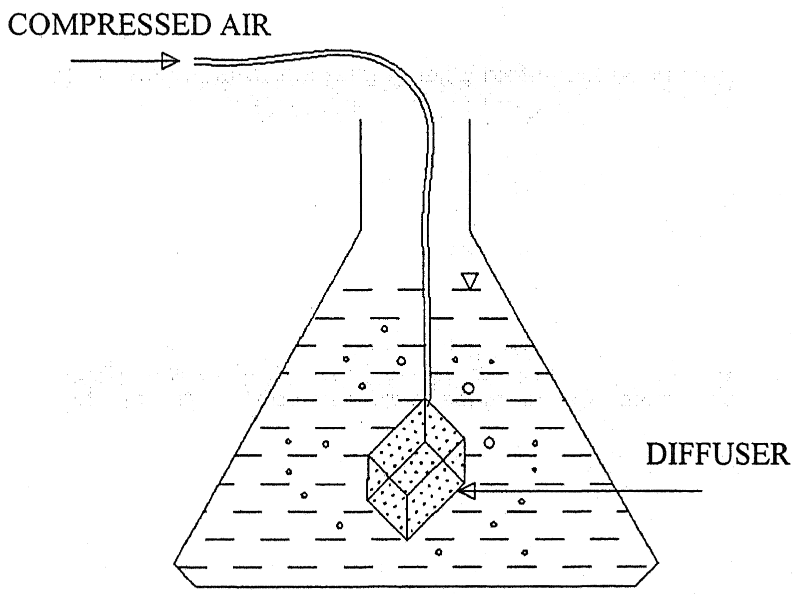


Figure 4.4: Schematic of Aerobic Reactor

Each reactor was started with different seed sludge. Aerobic Reactor (AR-I) was started directly with settled tannery wastewater. Aerobic Reactor (AR-II) and Aerobic Reactor

(AR-III) were initially seeded respectively with the activated sludge brought from the aeration tank of the CETP, Unnao and 130 MLD ASP based plant for domestic wastewater of Kanpur city at Jajmau to maintain an initial desired level of MLSS and MLVSS. Supernatant of settled tannery effluents were brought from the settling tank to feed the reactors. Air was supplied to each reactor through porous diffuser. The reactors were kept in a temperature controlled cabin maintained at 35 ± 0.5 °C. Once in each day, the air supply to the reactors was stopped and the sludge accumulated in the reactor was allowed to settle before removal of supernatant and addition of fresh settled tannery effluents. The hydraulic retention time for all three reactors were 1.25 days, i.e., 750 ml of substrate was added and 750 ml of settled effluent was removed daily from each reactor. The biological solids retention time in the reactors was very high since no sludge was wasted except for any inadvertent loss when settled effluent was removed each day. Monitoring was done by estimating COD, TSS, VSS, MLSS, MLVSS and pH in the feed and settled samples.

UASB Process: A laboratory scale up-flow anaerobic sludge blanket (UASB) reactor of capacity 30 liter with the main objective to assess the potential of anaerobic treatment for the removal of organics in settled tannery effluents was installed adjacent to the pilot-scale settling tank (Figure 4.3 and Table 4.1). The reactor was made of plexiglass. The reactor was initially seeded with sludge from UASB reactor of the CETP at Jajmau up to 50 cm height to achieve rapid start up. Reactor partially filled with sludge, was continuously supplied with settled tannery wastewater from feeding tank from the bottom of reactor by gravity. Feeding tank, capacity 200 liter was placed on the top of setting tank. Reactor was operated with solid retention time (SRT) 60 days and hydraulic retention time (HRT) 8 hours. The effluent of the reactor was collected in a tank (effluent collection tank). The grab and composite samples of both influent and effluent were prepared for analysis of TSS, VSS, COD (total and filtered), TOC, sulfate and chromium (total and filtered) analysis. Grab samples were analyzed for sulfide, temperature and pH just after the collection. Sludge samples taken from sludge blanket of the reactor were analyzed for TSS and VSS.

Table 4.1: Description of the Pilot-Scale UASB Reactor

Item	Shape	Diameter, mm	Height, mm
Reactor	Cylindrical	150 & 200	1500
Sludge Blanket Zone	Cylindrical	150	500
Zone of Reaction	Cylindrical	150	400
Settling Zone	Cylindrical	200	350

4.1.5 Anaerobic Digestion of Primary Sludge

Four Anaerobic Sludge Digesters, namely ASD-I, ASD-II, ASD-III and ASD-IV, each with the capacity of two liter (refer Figure 4.5) were setup to study the feasibility of degradation of primary sludge (sludge from settling tank). All the digesters were initially filled with sludge from UASB reactors of the CETP at Jajmau. The digesters were kept in a temperature controlled cabin maintained at 35 ± 0.5 °C and were operated in semi-continuous mode. ASD-I, ASD-II, ASD-III and ASD-IV were operated with solid retention time 20, 40, 50 and 60 days respectively, i.e. 100, 50, 40 and 33.3 ml were extracted daily after mixing the whole contents and the same quantities of undigested sludge (primary sludge) were added to respective digesters. Arrangements were also made to estimate total and methane gas content. Both influent and effluent were analyzed for TSS, VSS, pH, temperature, TA and VFA.

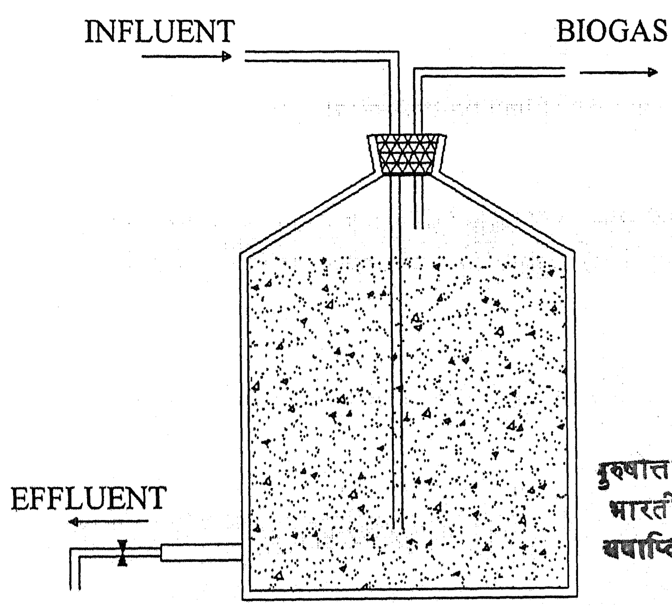


Figure 4.5: Schematic of Anaerobic Reactor

4.2 Analytical

Most of the analytical techniques followed were of routine type and were conducted as per the Standard Methods for the Examination of Water and Wastewater (APHA, *et al.*, 1995). A listing of such techniques along with instruments used, name of the method, reference, etc. are presented in Table 4.2

Table 4.2: Analytical Methods Employed for Estimation of Various Parameters

Test Parameter	Method Used	Instrument Used	Reference
pH	Combination pH Electrode	pH Meter, Toshniwal CL-51, India	Standard Methods, APHA *et al.* (1995)
TSS	2540D		Standard Methods, APHA *et al.* (1995)
VSS	2540G		Standard Methods, APHA *et al.* (1995)
Dissolved Oxygen, DO	Winkler's Method with Azide Modification		Standard Methods, APHA *et al.* (1995)
Biochemical Oxygen Demand, BOD	Incubation at 20°C for 5 days and DO Estimation as Above		Standard Methods, APHA *et al.* (1995)
Chemical Oxygen Demand, COD	Open Reflux Method	COD Reactor, HACH, USA	Standard Methods, APHA *et al.* (1995)
TOC	Oxidation at High Temperature	Total Carbon Analyzer, Model TOC-V $_{CPN}$, Shimadzu Make	Standard Methods APHA, *et al* (1995)
Sulfate	Colorimetric, Turbidity Method	4 cm cell, 420nm Spectrometer	Standard Methods APHA, *et al.* (1995)
Sulfide	Iodometric Method		Standard Methods APHA, *et al.* (1995)
VFA	Direct Titration		Dilallo and Albertson (1961)
Total Gas	Liquid Displacement (Figure 4.6)		
Methane Gas	Liquid Displacement using KOH Scrubber for CO_2 (Figure 4.7)		
Chromium	Filtration Through 0.2 µm Filter for Soluble Fraction and Acid Digestion Followed by Filtration Through 0.2 µm Filter for Total Chromium	Varian AAS, 220FS	Standard Methods APHA, *et al.* (1995)

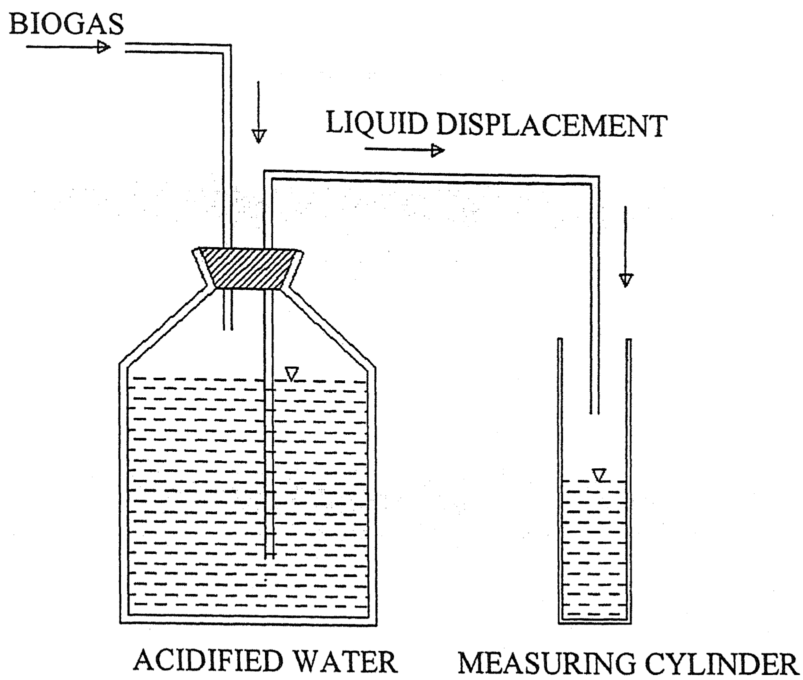


Figure 4.6: Experimental Setup for Total Gas Measurement

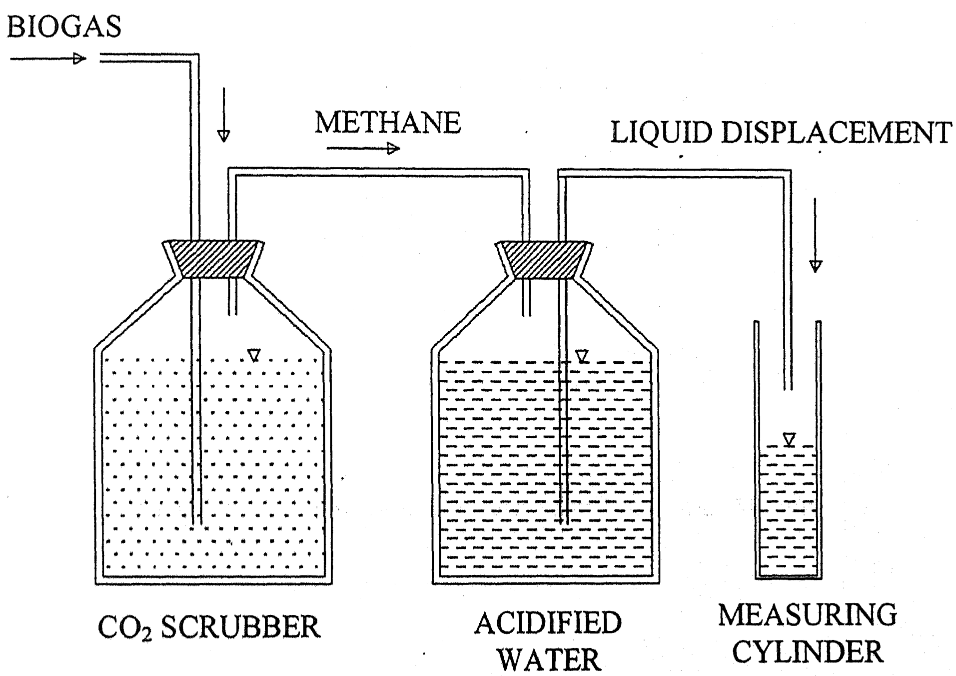


Figure 4.7: Experimental Setup for Methane Measurement

5. Results and Discussion

5.1 Genesis and Hypothesis

The concept of Common Effluent Treatment Plant (CETP) is gaining popularity for the cluster of Tanneries. In this individual tanneries are expected to discharge effluents after chrome recovery and primary treatment. The CETP typically is expected to focus on reduction in organic matter as represented by BOD and COD. For this conventional biological processes such as aerobic (Activated Sludge Process or its variants, ASP) or anaerobic (Upflow Anaerobic Sludge Blanket, UASB) are considered to be the most preferred options. However, CETPs based on either of these two options have not been able to reduce environmental problems substantially. Specifically, one of the major CETP based on UASB concept at Jajmau, Kanpur, UP, India is reported to perform poorly. The failure to give desired performance is generally attributed to the non-functioning of chrome recovery and primary treatment at the individual tanneries, and poor operation and maintenance of the CETP.

The genesis of the present study was the reported failure of the CETP, and more significantly the analysis of failure based on intuition rather than scientific investigations. Research work presented in this thesis postulated that the failure is due to the inappropriate application of process concept, and that the conventional biological processes have insignificant potential for the treatment of tannery effluents.

In order to support the aforementioned postulate, studies were carried out to investigate: (i) several aspects of the UASB based CETP at Jajmau, Kanpur, UP, India from concept to the present status, (ii) plausible changes in the characteristics of tannery effluents due to changes in practices adopted in tanning industries, (iii) implications of carrying out primary treatment in the CETP, (iv) potential of both conventional aerobic and anaerobic processes for the treatment of settled tannery effluents, and (v) feasibility of anaerobically stabilizing the primary sludge obtained from tannery effluents.

5.2 Efficacy of UASB Reactor in CETP for Tannery Effluents

A detailed study from the concept to the present status of the CETP at Jajmau, Kanpur, UP, India was carried out to investigate the suitability of UASB for treatment of tannery effluents. The concept of UASB in CETP was adopted based on the reported success of a 5000 m^3/d pilot plant for domestic wastewater at Jajmau, Kanpur, UP, India and the pilot studies conducted by Central Leather Research Institute in Kanpur (CLRI, 1988) to treat a mixture of primary treated tannery effluent and domestic wastewater. These studies concluded that UASB process can be advantageously applied in CETP to treat a mixture of tannery effluents, after chrome recovery and primary treatment in individual tanneries, and domestic wastewater of Kanpur city reaching the site in proportion of 1:3. Accordingly a CETP designed as per the flow sheet presented in Figure 4.1 was commissioned in 1994. A thorough mixing of the tannery effluents reaching the CETP in equalization tank was envisaged to avoid settling of suspended solids. Also, the primary settling of domestic wastewater was not included. It was envisaged that the suspended solids reaching the UASB reactor will promote formation of sludge blanket in addition to savings in cost incurred due to primary treatment in CETP. The UASB reactors were started by feeding domestic wastewater of Kanpur city without any external seeding or mixing with tannery effluents. Gradually the tannery effluents were introduced alongwith domestic wastewater until the ratio of 1:3 i.e. 9 mld tannery effluents and 27 mld domestic wastewater as suggested by CLRI studies was achieved. A number of performance monitoring programmes were conducted during and after the commissioning of the UASB reactors in the CETP.

Tables 5.1 and 5.2 present the summary of the performance of the UASB reactors during commissioning and post commissioning period respectively. Performance at a glance, in terms of the range in percent reduction in key parameters as presented in Table 5.3, clearly suggests poor performance, particularly in terms of filtered BOD and COD reduction. It is important to note that influent filtered BOD and COD values are in the range generally observed for domestic wastewater in Indian cities. Also, the change in the influent filtered BOD and COD to the UASB reactors during the commissioning period as the proportion of tannery influent increased from 0:1 to 1:5 is insignificant (refer Table 5.1).

Table 5.1: Summary of the Performance of UASB Reactors in CETP at Jajmau, Kanpur, UP, India During Commissioning (Source: UP Jal Nigam, 1994)

Parameters	TWW:DWW = 0:1			TWW:DWW = 1:16			TWW:DWW = 1:10			TWW:DWW = 1:7			TWW:DWW = 1:5		
Flow (MLD)	14.38±4.0 [12]			28.45±8.7 [4]			29.03±7.06 [7]			30.39±5.69 [7]			20.75±5.6 [11]		
HRT (hrs)	11.24±4.9 [12]			10.98±3.79 [4]			10.49±2.74 [7]			9.88±2.55 [7]			15.45±6.5 [11]		
	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal
Temp (^{0}C)	27.71±0.85 [7]	27.94±0.66 [7]		27.91±0.6 [11]	28.23±0.6 [11]		28.1±0.93 [6]	28.42±0.93 [6]		29.94±0.62 [7]	30.17±0.69 [7]		28.42±0.43 [4]	28.58±0.55 [4]	
pH	8.44±0.42 [9]	7.62±0.48 [9]		8.53±0.2 [11]	7.52±0.1 [11]		8.42±0.22 [6]	7.47±0.22 [6]		8.26±0.08 [7]	7.29±0.08 [7]		7.92±0.42 [4]	7.32±0.19 [4]	
FBOD (mg/L)	208.0±0 [1]	160.0±0 [1]	23.08±0 [1]	185.5±50.2 [2]	108.5±19.1 [2]	40.73±5.75 [2]	174±12.7 [2]	97±9.9 [2]	44.31±1.62 [2]	182.5±31.8 [2]	103±18.4 [2]	43.58±0.24 [2]	247±0 [1]	155±0 [1]	37.25±0 [1]
TBOD (mg/L)	383.0±79.2 [4]	175.5±52.3 [4]	54.26±9.23 [4]	330.5±74.2 [2]	184.5±91.2 [2]	45.91±15.4 [2]	319±15.6 [2]	127.8±15.9 [2]	60.03±3.04 [2]	386±15.6 [2]	137.2±45.6 [2]	64.65±10.4 [2]	468±0 [1]	189.5±0 [1]	59.51±0 [1]
FCOD (mg/L)	373.2±92 [12]	206.0±72 [12]	41.93±23 [12]	286.9±137 [7]	225.4±77.7 [7]	17.89±27.9 [7]	338.7±87.4 [7]	252.2±76.7 [7]	26.04±12.3 [7]	366±90.7 [6]	256.1±48.2 [6]	28.51±9.51 [6]	552.5±22.6 [4]	315.4±41.6 [4]	43.05±5.9 [4]
TCOD (mg/L)	780.6±163 [12]	345.5±100 [12]	53.73±18 [12]	798.5±594 [8]	283.1±102 [8]	54.73±21.0 [8]	821.9±168 [7]	372.4±80.1 [7]	54.53±6.1 [7]	838.4±81.1 [7]	368±54.9 [7]	56.15±5.19 [7]	1131±132 [4]	443.1±13.5 [4]	60.55±3.2 [4]
TSS (mg/L)	515.9±138 [7]	158.7±96.7 [7]	69.00±17.7 [7]	732.9±289 [7]	239.2±47.5 [7]	65.07±9.06 [7]	936.7±531 [7]	256.3±202 [7]	74.49±4.3 [7]	815.8±246 [6]	212.5±95.9 [6]	74.56±4.44 [6]	1199±235.5 [4]	302.5±58.3 [4]	74.65±2.23 [4]
VSS (mg/L)	125.7±98.2 [7]	55.71±23.4 [7]	35.65±41.2 [7]	295.9±155 [7]	93.71±30.0 [7]	62.36±16.2 [7]	421.6±133 [5]	154.8±84.9 [5]	64.53±12.1 [5]	424.2±78.6 [6]	119.3±25.4 [6]	71.85±3.06 [6]	376.2±62.5 [4]	111.9±8.98 [4]	69.66±5.33 [4]
VFA (mg/L)	5.09±2.31 [7]	3.87±1.74 [7]		2.20±0.33 [6]	1.09±0.55 [6]		2.62±0.76 [5]	1.08±0.12 [5]		2.46±0.75 [5]	0.96±0.17 [5]		3.1±0.1 [3]	1.13±0.1 [3]	
TALK (mg/L)	22.36±7.49 [5]	23.12±5.28 [5]		12.50±2.17 [6]	11.00±3.41 [6]		14.00±2.45 [5]	13.40±2.43 [5]		16.40±1.67 [5]	16.80±1.44 [5]		16.00±1 [3]	19.17±1.26 [3]	
Sulfate (mg/L)				91.12±70.9 [5]	66.60±50.4 [5]	25.75±7.2 [5]	119.8±125 [5]	76.96±65.1 [5]	30.48±7.56 [5]	110±0 [1]	55.5±0 [1]	49.54±0 [1]			
Sulfide (mg/L)				21±0 [1]	42±0 [1]		76.33±28.3 [3]	83.83±32.3 [3]		88.23±23.1 [6]	104.7±14.7 [6]		103.6±6.13 [4]	122.6±9.89 [4]	

Note: Values reported are average ± standard deviation based on the number of data points mentioned in the parenthesis

Table 5.2: **Summary of the Performance of UASB Reactors in CETP at Jajmau, Kanpur, UP, India During 1997-2002**
(Source: Tare, 1997; 1998; 1999; 2000; 2001; 2002)

Parameters	1997			1998			1999			2000			2001			2002		
Flow (Mld)	23.81±5.50 [54]			21.64±6.19 [38]			23.26±3.42 [48]			26.86±0.82 [5]			26.54±4.45 [33]			26.93±5.92 [48]		
HRT (hrs)	12.95±3.99 [54]			15.05±6.75 [38]			12.66±1.94 [48]			10.73±0.34 [5]			11.27±2.62 [33]			12.03±6.41 [48]		
	Inf	Eff	% Rem	Inf	Eff	% Rem	Inf	Eff	% Rem	Inf	Eff	% Rem	Inf	Eff	% Rem	Inf	Eff	% Rem
FBOD (mg/L)	211.3± 58.7 [54]	102.2± 44.3 [54]	51.73± 13.2 [54]	296.0± 63.9 [38]	161.8± 41.0 [38]	44.69± 11.5 [38]	288.9± 125 [48]	175.0± 76.6 [48]	41.40± 22.0 [48]	282.8± 48.8 [5]	186.0± 31.0 [5]	32.59± 15.2 [5]	324.2± 135 [33]	183.7± 73.1 [33]	41.92± 12.4 [33]	356.7± 127 [48]	215.5± 93.8 [48]	39.37± 15.7 [48]
TBOD (mg/L)	335.0± 94.2 [54]	150.1± 49.7 [54]	54.50± 10.0 [54]	444.6± 97.2 [38]	229.3± 46.9 [38]	47.58± 8.66 [38]	436.2± 134 [48]	238.5± 89.2 [48]	48.15± 16.2 [48]	505.2± 59.5 [5]	298.8± 76.7 [5]	40.99± 12.6 [5]	471.9± 180 [33]	262.4± 117 [33]	44.47± 10.3 [33]	565.2± 176 [48]	328.1± 122 [48]	42.18± 11.2 [48]
FCOD (mg/L)	405.4± 199 [54]	193.0± 82.1 [54]	49.82± 11.1 [54]	629.8± 717 [38]	273.8± 62.6 [38]	47.90± 8.81 [38]	447.0± 173 [48]	258.4± 104 [48]	41.21± 15.7 [48]	948.8± 50.2 [5]	661.6± 111 [5]	30.24± 11.4 [5]	642.5± 381 [33]	376.0± 181 [33]	37.50± 14.5 [33]	599.4± 197 [48]	373.5± 159 [48]	38.39± 14.4 [48]
TCOD (mg/L)	727.7± 319 [54]	326.4± 149 [54]	39.13± 24.0 [54]	882.0± 216 [38]	465± 103 [38]	46.69± 6.89 [38]	943.2± 302 [48]	436.2± 179 [48]	51.94± 16.0 [48]	1436 ±384 [5]	743.5± 174 [5]	45.74± 16.7 [5]	1061 ±417 [33]	537.2± 204 [33]	47.45± 13.0 [33]	1270 ±720 [48]	649.1± 268 [48]	44.63± 13.6 [48]
TSS (mg/L)	687.1± 211 [54]	382.7± 86.2 [54]	44.3±	788.9± 235 [38]	372.4± 85.4 [38]	49.02± 15.6 [38]	1040 ±887 [48]	361.5± 323 [48]	54.97± 26.0 [48]	1198 ±417 [5]	356.8± 218 [5]	67.73± 19.0 [5]	876.0± 255 [33]	348.6± 149 [33]	58.73± 15.3 [33]	867.8± 286 [48]	480.8± 190 [48]	44.70± 11.9 [48]
VSS (mg/L)										651.2± 147 [5]	244.8± 157 [5]	59.33± 29.1 [5]	478.4± 187 [33]	235.8± 146 [33]	51.41± 17.9 [33]	473.0± 140 [48]	265.2± 113 [48]	44.63± 12.5 [48]

Note: Inf – Influent; Eff – Effluent; Rem – Removal; Values reported are average ± standard deviation based on the number of data points mentioned in the parenthesis.

This reveals that the change in the concentration of soluble organic matter due to the addition of tannery effluents is insignificant.

Table 5.3: Performance at Glance of UASB Reactors in CETP at Jajmau, Kanpur, UP, India during Commissioning and Post Commissioning Period

Parameter	During Commissioning	Post Commissioning
Filtered BOD	23 - 44	33 - 52
Total BOD	46 - 65	41 - 54.5
Filtered COD	18 - 43	30 - 50
Total COD	54 - 61	39 - 52
Total Suspended Solids	65 - 75	44 - 68
Volatile Suspended Solids	36 -72	45 - 59

Note: Values in the table represent range in percent reduction

To further investigate the performance of the UASB reactors, an independent study was carried out for one year during June 2003 – July 2004 as part of this research. The results are presented in Figure 5.1. An analysis of the performance data has been presented in Table 5.4. The performance analysis carried out compares well with the reported performance data (refer Tables 5.2 and 5.3) suggesting that the UASB reactors consistently under performed since commissioning. In order to compare the observed performance with the estimates made while designing the plant, the data regarding the anticipated design performance is included in Table 5.4. Comparison of the design data with the observed performance analysis data reveals that the contribution of total organic matter as represented by BOD and COD values from tannery effluents is much below the expected levels. Particularly, the contribution in the concentration of soluble organics from tannery effluents is marginal. Interestingly, the tannery effluents substantially increased the sulfate and sulfide levels when mixed with domestic wastewater. It is well documented in the literature that sulfate and sulfide adversely affect the methanogenesis (Patidar, 2001). This is substantiated by much less ($\approx$ 16 %) gas production compared to anticipated (refer Table 5.4).

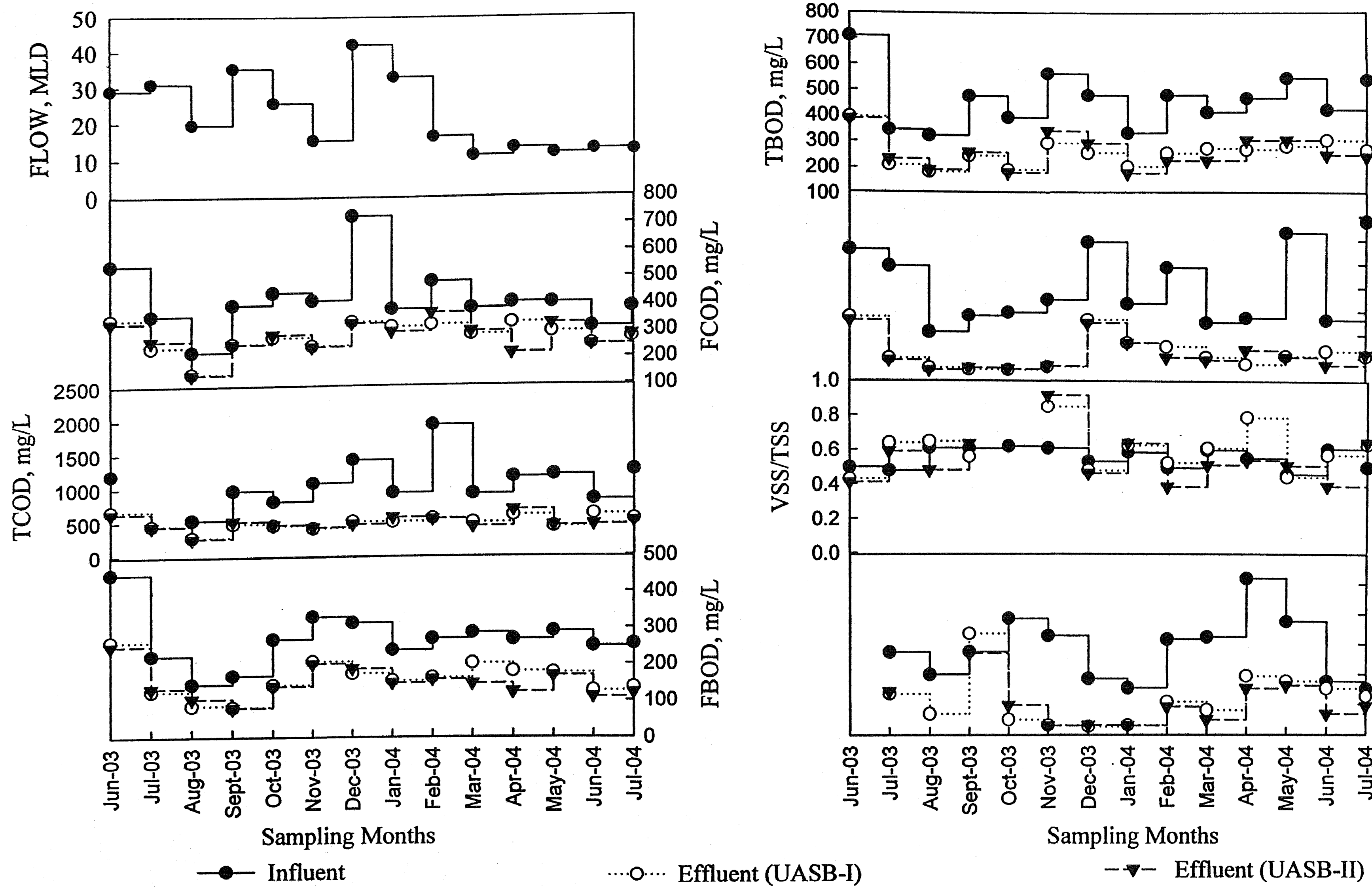


Figure 5.1: Performance of UASB Reactors in CETP at Jajmau, Kanpur, UP, India

Table 5.4: Comparative Evaluation of Design and Actual Performance (Based on Monitoring Done during 2003-2004) of UASB Reactors in CETP at Jajmau, Kanpur, UP, India

Parameters	Anticipated Design Performance			Actual Performance		
Flow, MLD	36.0			23±10.4(44)		
HRT, h	8			15.3±7.0(44)		
	Inf	**Eff**	**% Removal**	**Influent**	**Effluent**	**% Removal**
pH				7.78±0.38 (41)	7.45±1.23	
TCOD, mg/L	1875	600	68	1083.3±383.8 (46)	513.9±105.3	53.6±11.6
FCOD, mg/L				427.5±136.4 (46)	301.0±66.0	28.5±12.5
TBOD, mg/L	775	175	77	463.2±124.6 (46)	258.3±69.5	43.6±10.7
FBOD, mg/L				266.3±91.0 (46)	156.5±53.7	42.5±10.1
TSS, mg/L	1625	570	65	824.2±402.0 (46)	262.1±151.7	66.7±13.5
VSS, mg/L				440.0±174.00 (46)	149.5±65.5	64.1±13.1
Sulfide, mg/L				39.5±15.1 (11)	126.7±39.1	67.3±13.1
Sulfate, mg/L				592.0±245.9 (23)	219.4±184.2	58.8±37.4
Biogas, m^3/h	75.0			12.5		

Note: Inf – Influent; Eff – Effluent; Values reported are average ± standard deviation based on the number of data points mentioned in the parenthesis

Some studies have argued that the poor performance of the UASB reactor is due to inefficient chrome recovery and primary treatment at individual tanneries resulting in high amount of chromium in the tannery effluents reaching the CETP (Rajeswari, 1998; Qureshi and Dixit, 2003). The analysis of the sludge obtained from the UASB reactors indicates substantial amount of chromium (refer Figure 5.2). However, much of the chromium present is in insoluble form and as fraction of TSS it is insignificant. While this sludge is potentially hazardous due to possible conversion of trivalent chromium to hexavalent chromium, the fresh sludge does not contain significant amount of hexavalent chromium that could adversely affect the methanogenesis (Gupta, 2000; Verma, 2002; Tare *et al.*, 2003). Further high amount of TSS accompanied by high VSS/TSS ratio suggests presence of substantial amount of suspended organics in the UASB sludge (refer Figure 5.2). Much of these organics are

contributed by tannery effluents and may not indicate high levels of biomass in the UASB reactors.

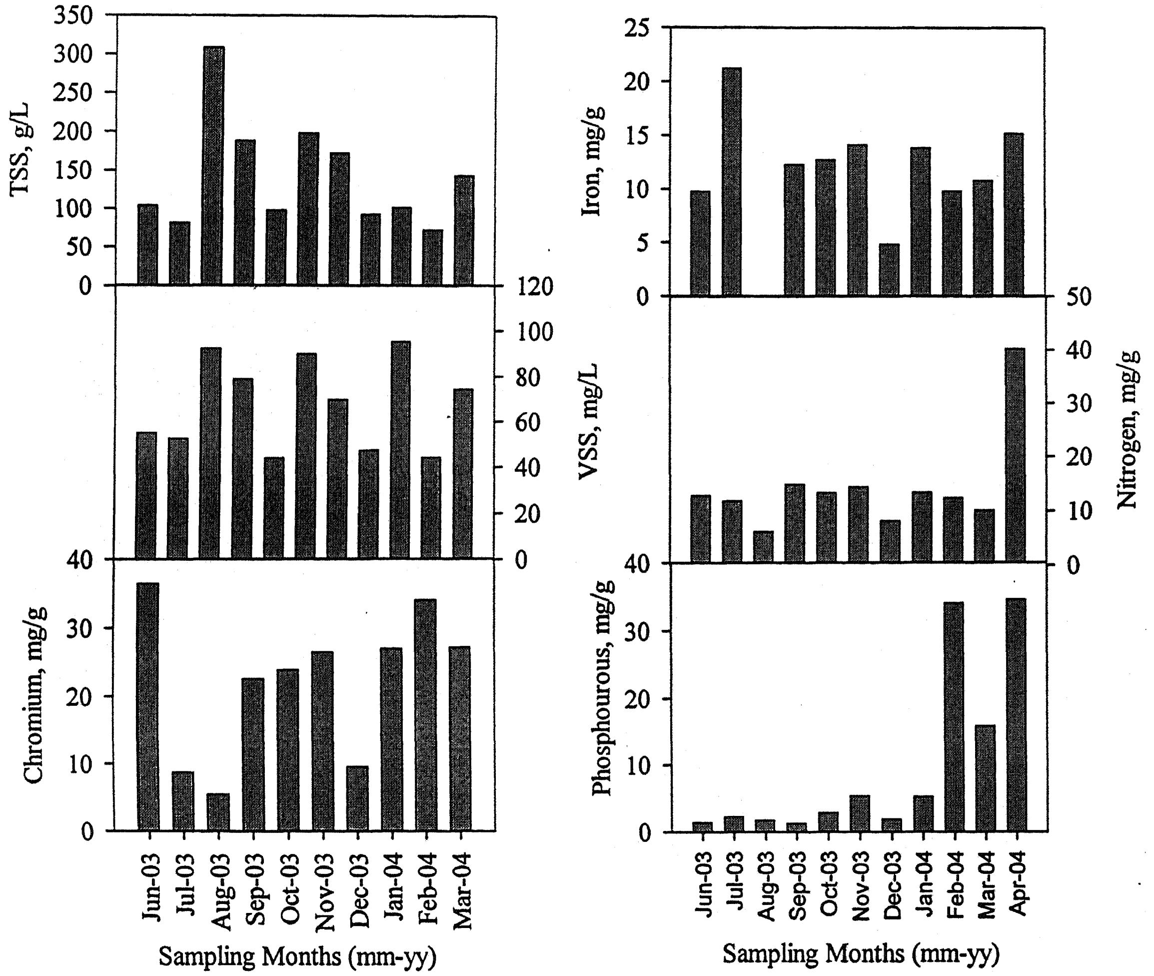


Figure 5.2: Characteristics of the Sludge Withdrawn from UASB Reactors in CETP at Jajmau, Kanpur, UP, India

A COD balance, based on the data and assumptions given in Table 5.5, reveal that insignificant portion of the influent COD is converted to methane COD (refer Figure 5.2).

Table 5.5: Estimated Values of Various Parameters Used in COD Balance for UASB Reactors in CETP at Jajmau, Kanpur, UP, India for December 2003 and June 2004*

Parameter	December 2003	June 2004
Average temperature	12-18 ^{0}C	24-26 ^{0}C
Average total flow, m^3/d	33.3x 10^3	31.0 x 10^3
Average influent TCOD, mg/L	925.0	906.5
Average effluent COD, mg/L	526.8	438.8
Total biogas production, m^3/day	300.00 m^3	500.00 m^3
Average methane content in biogas (Assumed)	80 %	80 %
Average SO_4 in influent, mg/L	310	548
Average SO_4 in effluent, mg/L	63.8	280.2
Average Sulfide in influent, mg/L	30	40
Average Sulfide in effluent, mg/L	98	110
Total Sludge discharged, m^3/d	248	248
Average COD of sludge, mg/L	45000	36000
Theoretical methane production	0.38 ml/mg of COD stabilized at 25^{0}C	0.38 ml/mg of COD stabilized at 25^{0}C
Solubility of methane in water, mg/L (Computed)	1.33 mmol/L	1.056 mmol/L

* Average values are based on 3 d and 4 d performance data for the months of December 2003 and June 2004 respectively

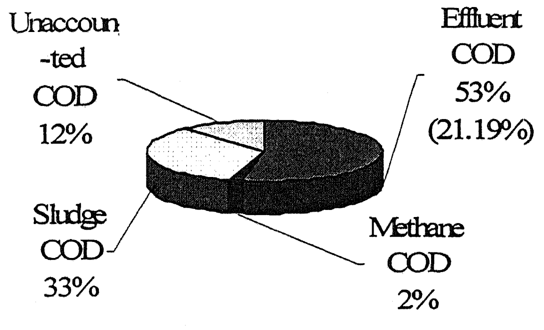
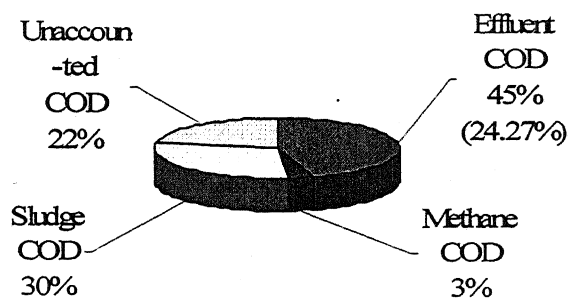
COD Mass Balance for December 2003	COD Mass Balance for June 2004
	
Total Influent COD = 30839.50 Kg/d (6.49%)	Total Influent COD = 28101.50 Kg/d (8.83%)
The values in the parentheses represents % COD due to sulfide.	

Figure 5.3: COD Balance for the UASB Reactors in CETP at Jajmau, Kanpur, UP, India

Data used for COD balance (refer Table 5.5) indicates that the COD channelized in reduction of sulfate is much higher (≈ 13-15 %) than that is gasified through methanogenesis (≈ 2-3 %). This suggests possible competition between methanogenesis and sulfidogenesis and resulting toxicity to both methanogens and sulfate reducers (Patidar, 2001). Thus this part of the investigation supports the postulate that the poor performance of the UASB reactors in CETP is to be primarily attributed to the biological limitations of methanogenesis rather than failure of pretreatment and poor operation and maintenance practices as generally believed.

5.3 Reappraisal of Tannery Effluents

This part of the study was conducted to investigate the changes that may have occurred in the characteristics of the tannery effluents due to the plausible changes in the practices adopted in the tanneries over a period of past two decades i.e. from the conceptualization of the CETP. For this purpose characteristics of the tannery effluents reaching the two CETPs for different clusters of tanneries were analyzed extensively and compared with other estimates reported in literature. The results are summarized in Table 5.6

Table 5.6: Assessment of Changes in the Characteristic of Tannery Effluents

Parameters	Tannery Wastewater Characteristic				
	CLRI, 1988	CPCB, 1996		Present Study	
pH	8.2-9.2	9.7/9.8	9.5/8.75	8.00±0.30 (11)	
TSS		1117/2441	647/400	2417.8±1633.3 (13)	1862.7±864.9 (14)
VSS				1068.4±627.30 (11)	741.7±269.94 (14)
TCOD	4500-7500	1751/1824	1555/1154	2455.4±897.5 (22)	2077.7±644.3 (14)
FCOD	3000-4800			1064.6±474.2 (22)	1267.4±337.0 (14)
Sulfate	1540-3300			1169.0±398.5 (12)	
Sulfide				104.4±42.1 912)	
Chromium	1540-3300	28.3/53.3	14.8/23.1	213.2±110.7 (7)	
TOC				337.2±185.12 (11)	319.3±140.2 (14)

Note:

I. All parameters except pH are expressed in mg/L.

II. Data reported in CLRI, 1988 are based on a survey in the year 1988 to predict tannery effluent characteristic. Estimated values are given in a range.

III. Data reported in CPCB, 1996 is based on general performance study for one day (24 h composite) each in the months of Feb 1996 and May 1996.

IV. Values obtained from the present study are reported as average ± standard deviation with number of data points mentioned within the parenthesis.

V. Values in the last column are for Unnao, UP, India. All other values are for Jajmau, Kanpur, India.

Comparison of the characteristics obtained in the present study for the two different tannery clusters compare well with each other and those reported by CPCB (1996) considering the actual variations. The characteristics anticipated by CLRI (1988) assume higher values of COD than the actual observed in the present study. However, sulfate levels compare well with those obtained in the present study. In general it can be said that no significant changes have occurred in the characteristics of tannery effluents due to change in practices in the tanneries. Even if the actual characteristics would have remained same, the UASB process would have failed due to unfavorable COD:Sulfate ratio (Patidar, 2001). The analysis of the tannery effluents obtained in the present study clearly indicates that primary treatment may be advantageous due to

presence of substantial amount of suspended solids. Further the soluble organics appear to be much lower for any conventional biological process to be very effective.

5.4 Potential of Primary Treatment

The characteristic of the tannery effluents reaching the CETP suggest that primary treatment with or without the addition of coagulating agents may be beneficial. Hence, settling experiments at pilot and laboratory scale were conducted. Results are presented in Table 5.7 and Figure 5.4.

Table 5.7: Performance Analysis of the Pilot Scale Settling Tank for Treatment of Tannery Effluents Received at CETP, Jajmau, Kanpur, UP, India

Parameters	Influent	Effluent	% Removal
TSS (mg/L)	2417.8±1633.6	565.5±23.6	67.3±23.6
VSS (mg/L)	1068.4±627.3	306.9±206.5	63.86±24.8
VSS/TSS	0.36±0.17	0.44±0.21	
TCOD (mg/L)	2455.4±897.5	547.6±326.9	76.8±10.3
FCOD (mg/L)	1064.6±474.2	239.8±166.4	76.3±12.9
TOC (mg/L)	337.2±185.2	68.7±51.7	75.0±19.5
TCOD/TOC	11.9±11.2	11.5±7.1	
Chromium (mg/L)	213.2±110.7	63.8±55.8	65.9±29.0

Note: Values reported are average ± standard deviation based on 21-23 data points

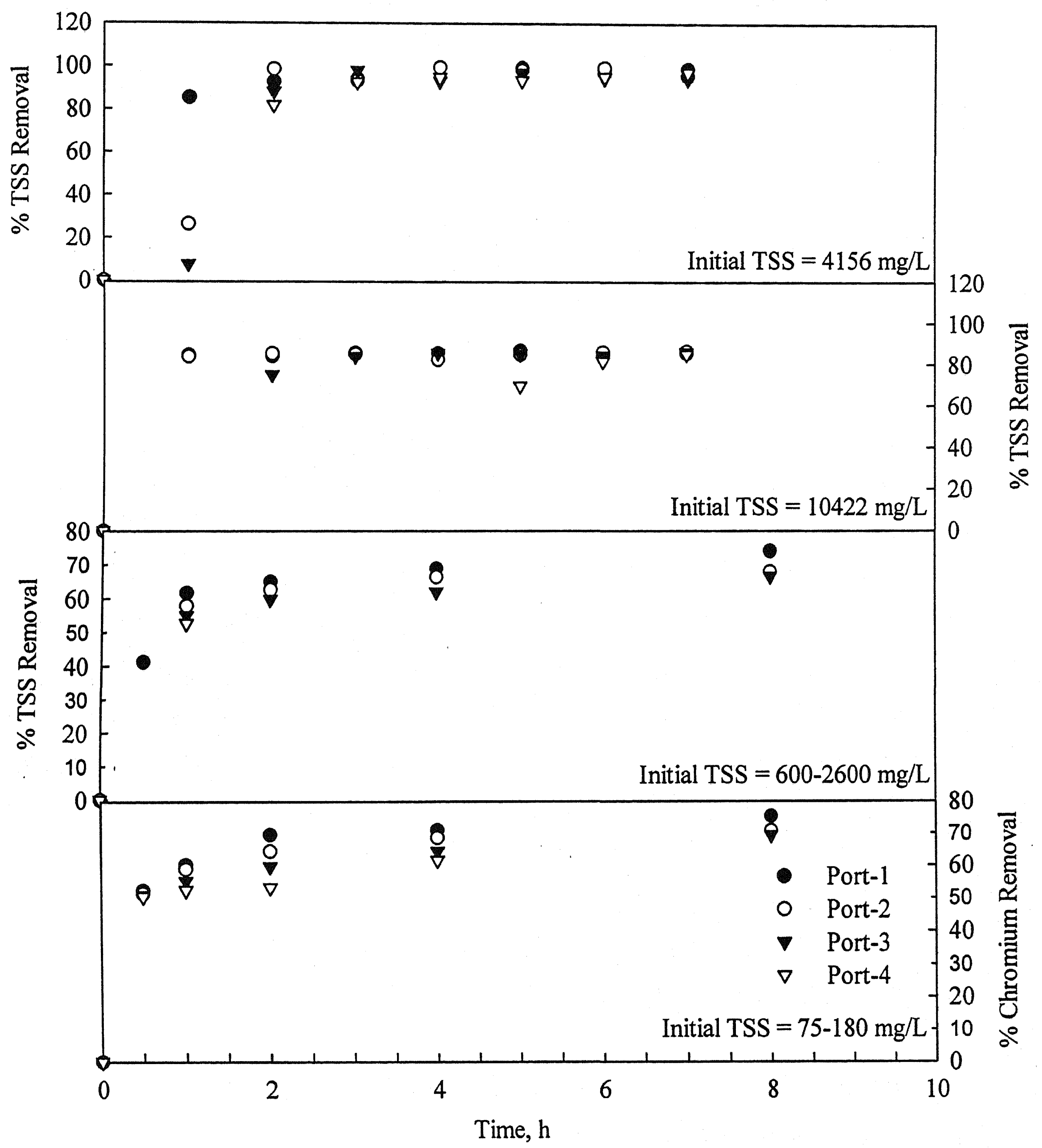


Figure 5.4: TSS and Chromium Removal from Tannery Effluents in Settling Column Experiments

The results suggest that primary treatment can achieve substantial reduction in organics and chromium. The removal efficiencies are comparable to the CETPs. This indicates that much of the removal in CETPs is due to settling and contribution of the

biological process is insignificant. This further supports the postulate that conventional biological processes do not contribute significantly in the treatment of tannery effluents reaching the CETP.

5.5 Potential of Conventional Biological Treatment Processes

In order to assess the potential of conventional biological processes widely used in CETPs for tannery effluents, laboratory scale studies were conducted employing both anaerobic and aerobic processes. The efficacy of these processes for the treatment of settled tannery effluents was evaluated through monitoring several process parameters.

5.5.1 Anaerobic Treatment

A laboratory scale model of UASB reactor seeded with sludge obtained from the full scale UASB reactor treating mixture of domestic and tannery effluents, and fed with settled tannery effluent was operated for more than six months in a continuous mode. The reactor was operated at an HRT 8 h and an upflow velocity 0.19 m/h. Performance analysis results are presented in Table 5.8. Substantial removal in TSS and VSS was observed. However, total COD removal was less and filtered COD removal was much less. Higher removal of VSS but low COD removal indicates contribution of COD due to appearance of sulfides in the effluent (refer Table 5.8). Sulfides may have adversely affected methanogenesis (Patidar, 2001). The COD:Sulfate ratio in the settled tannery effluents is highly unfavorable for methanogenesis (Patidar, 2001). The gas production was negligible suggesting that methanogenesis was inhibited due to sulfide toxicity. Much of the removal of TSS and VSS could be attributed to settling and trapping in the sludge blanket.

Overall the performance studies reveal that UASB process is unsuited for the treatment of settled tannery effluents. Synthesis of the results of the studies presented in previous sections with that of the performance of the laboratory scale UASB presented in Table 5.8, it can be inferred that failure of UASB reactors in CETP for

tanneries is essentially due to inability of the biological system employed rather than inefficient pretreatment or inadequate operation and maintenance practices.

Table 5.8: Performance Analysis of the Laboratory Scale UASB Reactor Treating Settled Tannery Effluents Received at CETP, Jajmau, Kanpur, UP, India

Parameter	Influent	Effluent	% Removal
Temp	32.7±4.2^{0}C	32.3±3.7^{0}C	
pH	8.0±0.3	8.0±0.1	
TSS (mg/L)	565.5±23.6	152.8±62.6	60.5±22.7
VSS (mg/L)	306.9±206.5	99.0±51.7	59.6±22.5
VSS/TSS	0.4±0.2	0.6±0.2	
TCOD (mg/L)	547.6±326.9	368.0±204.6	26.2±26.5
FCOD (mg/L)	239.8±166.4	199.4±77.6	6.4±40.3
TOC (mg/L)	68.7±51.7	64.58±42.68	5.99±10.33
Sulfate (mg/L)	1467.0±418.5	1255.2±384.4	
Sulfide (mg/L)	23.2±16.2	93.8±69.9	

Note: Values reported are average ± standard deviation based on 21-23 data points

5.5.2 Aerobic Treatment

Three aerobic suspended growth reactors fed with settled tannery effluents were operated over a period of 75 d. In the first reactor (AR-I) no external seed was introduced. The second reactor (AR-II) was seeded with sludge obtained from the ASP based CETP for tanneries. The third reactor (AR-III) was seeded with ASP based treatment plant for domestic wastewater. Biomass development was very slow in AR-I. The MLSS concentration gradually decreased in AR-II and AR-III indicating wash out of biomass. The course of performance parameters of the aerobic reactors is presented in Figure 5.5 and a summary of the performance analysis is given in Table 5.9. Results indicate very less removal of soluble organics. The slight removal of filtered BOD may be attributed to the oxidation of sulfides. In general based on the

results of the present studies it can be inferred that aerobic suspended growth systems are most inappropriate for the degradation of organics in settled tannery effluents. As such application of ASP in CETP for tanneries proves to be futile. This further strengthens the hypothesis that conventional biological treatment processes are ineffective for the treatment of tannery effluents.

5.6 Stabilization of Primary Sludge

Attempts were made to study the digestion of primary sludge obtained from tannery effluents. Four anaerobic digesters with HRT 20, 40, 50 and 60 d were set up in semi-continuous mode, and were operated for more than 70 d. The course of parameters for various performance indicators is presented in Figure 5.6. A summary of the analysis of the performance results is presented in Table 5.10. Overall it can be inferred that none of the digesters could sustain methanogenesis and hence it is unlikely that primary sludge can be digested anaerobically in an effective manner. Sulfide levels were very high in all the digesters and hence methanogenesis may have ceased due to toxicity from sulfides (Patidar, 2001). The toxicity effect due to sulfides in anaerobic digesters used in the presents study appears to be much higher than the UASB reactors in CETP, Jajmau, Kanpur, UP, India. This may be due to washout of the sulfides produced due to higher flow rate (low HRT: 8 h) in UASB reactors of CETP. In fact, much of the gas produced in CETP is due to hydrolysis and gasification of suspended organics rather than from soluble organics. Thus alternative strategy needs to be evolved for the digestion of primary sludge obtained from tannery effluents.

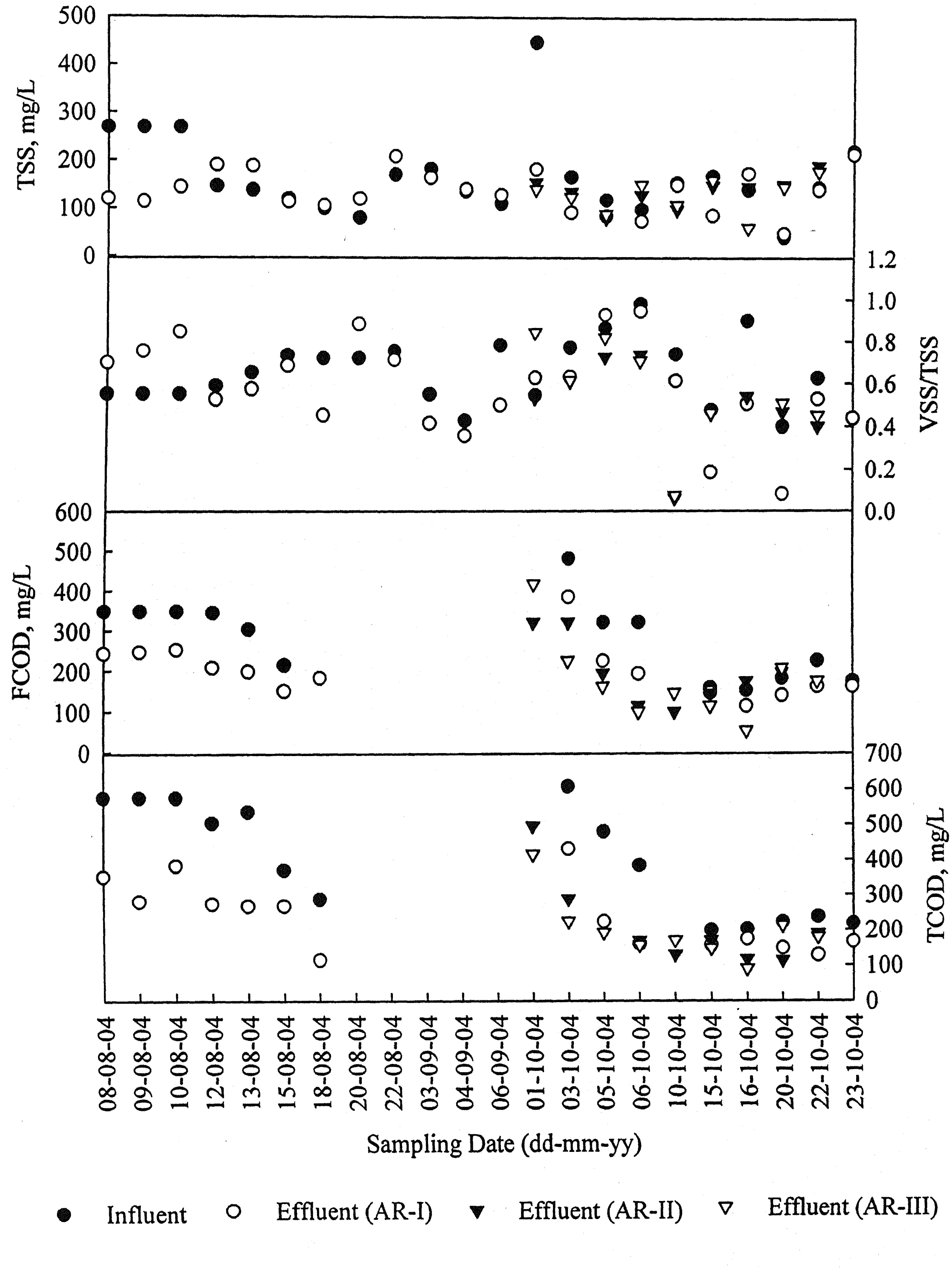


Figure 5.5: Course of Performance Parameters of Aerobic Suspended Growth Reactors Fed with Settled Tannery Effluents

Table 5.9: Performance Analysis of Aerobic Suspended Growth Reactors Treating Settled Tannery Effluents Received at CETP, Jajmau, Kanpur, UP, India

Parameters	AR-I			AR-II			AR-III		
	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal
pH	8.1±0.4	8.76±0.41		8.1±0.4	8.0±0.4		8.1±0.4	8.4±0.7	
TSS	144.3±58.8	135.3±60.0	2.10±26.0	144.3±58.7	127.0±49.0	7.0±21.7	144.3±58.8	133.7±42.8	10.4±29.47
VSS	87.0±38.6	61.3±40.5	37.4±32.4	87.0±38.5	53.0±38.3	45.7±31.7	87.0±38.6	59.0±39.7	33.0±30.2
TCOD	215.1±15.8	154.7±17.9	27.4±12.6	215.1±15.8	143.4±33.8	32.7±17.8	215.1±15.8	159.4±45.3	25.8±19.8
FCOD	176.8±28.9	142.8±19.8	18.6±10.0	176.8±28.9	155.7±37.4	12.2±15.1	176.8±28.9	137.0±59.0	22.8±28.8
TBOD	144.4±31.4	88.4±25.8	39.0±8.1	144.4±31.4	54.4±13.9	60.6±12.9	144.4±31.4	71.2±28.2	50.0±20.2
FBOD	85.2±32.8	32.0±16.4	62.8±9.4	85.2±32.8	36.4±13.1	53.8±20.2	85.2±32.8	43.6±16.8	46.2±18.3
Sulfide	59.8±32.1	10.0±8.2	86.2±8.0	59.8±32.1	16.2±5.7	66.3±16.8	59.8±32.1	14.8±6.9	76.5±3.8
Sulfate	1326.9±209.2	1445.1±171.9		1326.9±209.2			1326.9±209.2		
MLSS	1340.0			1167.8			1640		
MLVSS	840.0			130.5			1340		

Values reported are average ± standard deviation based on the last 6-8 data points; All parameters except pH are expressed in mg/L; AR-I was started without any external seed; AR-II was seeded with sludge obtained from ASP based CETP at Unnao, UP, India; AR-III was seeded with sludge obtained from ASP based domestic wastewater treatment plant at Jajmau, Kanpur, UP, India

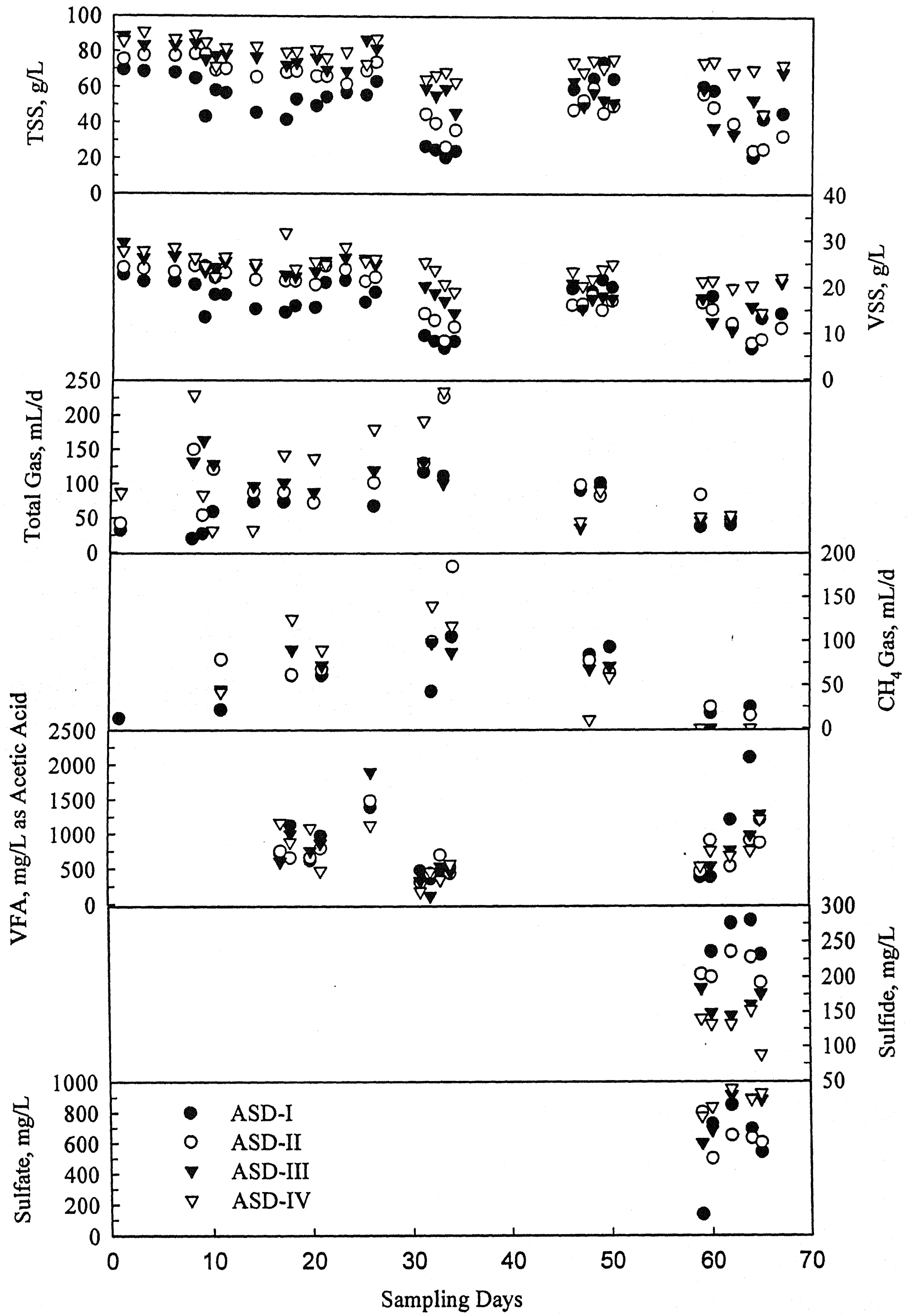


Figure 5.6: Course of Performance Parameters of Anaerobic Digesters for Stabilization of Primary Sludge Obtained from Tannery Effluents

Table 5.10: Performance Analysis of the Laboratory Scale Anaerobic Digesters for Stabilization of Primary Sludge Obtained by Settling Tannery Effluents Received at CETP, Jajmau, Kanpur, UP, India

Parameters	Characteristic Value in Various Digesters			
	ASD-I (HRT: 20 d)	ASD-II (HRT: 40 d)	ASD-III (HRT: 50 d)	ASD-IV (HRT: 60 d)
pH	8.1±0.2	8.4±0.3	8.5±0.3	8.5±0.3
TSS, mg/L	44.8±14.4	38.1±12.9	49.8±13.2	67.7±11.3
VSS/TSS	0.3±0.0	0.3±0.0	0.3±0.0	0.3±0.0
Total Gas, mL/d	38.5±2.1	65.5±26.2	45.8±1.1	52.0±1.4
CH_4 Gas, mL/d	21.5±5.0	20.0±7.1	0.0±0.0	0.0±0.0
VFA, mg/L as Acetic Acid	1050.0±717.4	727.5±221.2	810.0±320.0	780.0±252.1
Sulfide, mg/L	245.6±32.1	212.0±19.0	162.4±17.3	128.8±24.2
Sulfate, mg/L	589.9±276.8	638.4±109.2	795.0±142.5	875.3±71.3

Note: Values reported are average ± standard deviation based on the last 6-8 data point

6. Epilogue

The concept of Common Effluent Treatment Plant (CETP) is gaining popularity for the cluster of Tanneries. The CETP typically is expected to focus on reduction in organic matter as represented by BOD and COD. For this conventional biological processes such as aerobic (Activated Sludge Process or its variants, ASP) or anaerobic (Upflow Anaerobic Sludge Blanket, UASB) are considered to be the most preferred options. The genesis of the present study was the reported failure of the CETP, and more significantly the analysis of failure based on intuition rather than scientific investigations. In this research it was postulated that the failure is due to the inappropriate application of process concept, and that the conventional biological processes have insignificant potential for the treatment of tannery effluents.

In order to support the aforementioned postulate, studies were carried out to investigate: (i) several aspects of the UASB based CETP at Jajmau, Kanpur, UP, India from concept to the present status, (ii) plausible changes in the characteristics of tannery effluents due to changes in practices adopted in tanning industries, (iii) implications of carrying out primary treatment in the CETP, (iv) potential of both conventional aerobic and anaerobic processes for the treatment of settled tannery effluents, and (v) feasibility of anaerobically stabilizing the primary sludge obtained from tannery effluents.

Based on the synthesis of the available information and the results obtained in the present studies, following inferences may be drawn.

- Performance of the UASB reactors in CETP for tanneries at Jajmau, Kanpur, UP, is poor, particularly in terms of filtered BOD and COD reduction.
- The contribution of total organic matter as represented by BOD and COD values from tannery effluents is much below the expected levels. Particularly, the contribution in the concentration of soluble organics from tannery effluents is marginal. The tannery effluents substantially increase the sulfate and sulfide levels when mixed with domestic wastewater.

- Insignificant portion of the influent COD is converted to methane COD in UASB reactors in CETP for tanneries. The COD channelized in reduction of sulfate is much higher (≈ 13-15 %) than that is gasified through methanogenesis (≈ 2-3 %).
- Insignificant changes have occurred in the characteristics of tannery effluents due to change in practices in the tanneries. Primary treatment can achieve substantial reduction in organics and chromium. Much of the removal in CETPs is due to settling and contribution of the biological process is insignificant. Conventional biological processes do not contribute significantly in the treatment of tannery effluents reaching the CETP.
- The UASB process is unsuited for the treatment of settled tannery effluents. The failure of UASB reactors in CETP for tanneries is essentially due to inability of the biological system employed rather than inefficient pretreatment or inadequate operation and maintenance practices.
- In general, aerobic suspended growth systems are most inappropriate for the degradation of organics in settled tannery effluents. As such application of ASP in CETP for tanneries proves to be futile.
- It is unlikely that primary sludge obtained from tannery effluents can be digested anaerobically in an effective manner. The toxicity effect due to sulfides in anaerobic digesters may be much higher than the UASB reactors in CETP.
- Alternative strategies need to be evolved for the digestion of primary sludge obtained from tannery effluents. Anaerobic digestion of primary sludge after dewatering to remove substantial portion of sulfate and sulfide or vermicomposting of primary sludge after chromium removal by mixing with other organic matter such as animal dung or agricultural wastes for reuse and recovery of resources may be explored.

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